

Pt(0) microscrolls obtained on nickel surface by galvanic replacement reaction in H₂PtCl₆ solution as the basis for creating new SERS substrates

Maria V. Kaneva^a, Evgen V. Borisov^b, Valeri P. Tolstoy^c

Institute of Chemistry, Saint Petersburg State University, St. Petersburg, 198504, Russia

^askt94@bk.ru, ^beugene.borisov@spbu.ru, ^cv.tolstoy@spbu.ru

Corresponding author: Valeri P. Tolstoy, v.tolstoy@spbu.ru

PACS 82.33.Pt, 82.45.Mp, 82.45.Yz

ABSTRACT The paper explores the morphology features of Pt(0) nanolayers obtained on the surface of chemically polished nickel as a result of the galvanic replacement reaction using H₂PtCl₆ solution. In a series of samples synthesized at a treatment time of 1–60 minutes, it is shown that the nanolayers consist of Pt(0) nanocrystals 5–10 nm in size, which form a continuous porous layer with a thickness depending on the treatment time in solution. For example, it is about 80 nm and 120 nm for samples obtained after 3 minutes and 20 minutes, respectively. Moreover, on the outer side of the nanolayer with respect to the substrate, these nanocrystals form arrays of pointed agglomerates directed along the normal to the surface. After drying in air, the Pt(0) nanolayer cracks and partially folded microscrolls form on the nickel surface, the number of which is the largest for the samples obtained with a longer treatment time. The features of the practical application of these samples as SERS substrates are studied using the Raman spectra of Rodamin 6G as an example. It is shown that the amplification factor is about 10⁵–10⁶ using 532 nm laser excitation.

KEYWORDS platinum, nanocrystals, microscrolls, galvanic replacement reaction, SERS.

ACKNOWLEDGEMENTS This work was supported by the RFBR grant (project # 20-33-90228/20-PhD-students). We are grateful to the “Centre for Optical and Laser Materials Research” and “Nanotechnology” Research Parks of Saint Petersburg State University, for their technical assistance with the synthesized samples investigation.

FOR CITATION Kaneva M.V., Borisov E.V., Tolstoy V.P. Pt(0) microscrolls obtained on nickel surface by galvanic replacement reaction in H₂PtCl₆ solution as the basis for creating new SERS substrates. *Nanosystems: Phys. Chem. Math.*, 2022, **13** (5), 509–513.

1. Introduction

Application of Raman spectroscopy to the study of organic molecules and biological objects is one of the most widely discussed topics in optical spectroscopy. To confirm it, one can mention that more than 300 reviews were published on this topic in 2021 according to international databases, for example [1–3]. One of the central questions for choosing the conditions for obtaining such spectra is the creation of optimal, so-called SERS substrates, which the investigated substance is applied on and which provide high values of the effective signal amplification factor [4–8].

To date, many methods of creating such substrates have been tried and are being used. The use of precious metals with nano- and microtubular morphology for this purpose is one of the directions of further development of the topic. In particular, in article [9], microtubes of gold with a length of several microns and a diameter of 0.5 to 3.5 μm with a wall thickness of several tens nm were obtained. The walls of these microtubes have a relatively large proportion of atoms on the surface and exhibit SERS signals nearly 20 times larger than those of the gold film. A similar SERS signal reinforcement effect was also found in the case of Au nanoparticles applied to the inner surface of microtubes with walls made of InGaAs/GaAs layers [10]. The original way of producing Au microtubes was proposed in the work [11]. For this purpose, nanoparticles Au were adsorbed on the surface of the *Trichoderma asperelum* and *Aspergillus sydowii* fungi and then the biological material was removed by solvent washing and heating in the air at 400°. The walls of the microtubes produced under these conditions were found to consist of nanoparticles Au with a size of about 20 nm and the microtubes were 2–4 μm in diameter and several tens of μm in length. Moreover, the position of the maximum light absorption band Au lies in the range of 680 to almost 1000 nm and depends on the ratio of the diameter and length of the tube.

The last circumstance makes it possible to focus on specimens that provide maximum amplification of the useful signal in SERS. It should also be noted that the work [12] in which the authors studied the optical properties of microtubes with walls of Ag obtained by the method of template - synthesis using a solution of the mixture AgNO₃ and Na-cit and porous membrane of polycarbonate. These microtubes had a diameter of about 3–4 μm, a length of about 10 μm and a wall thickness of several tens of nanometers. They have been found to exhibit SERS substrate properties in the production of Raman spectra of Rhodamine 6G molecules.

It is noteworthy to mention the work [13] devoted to fabrication of Ag-SiO_x microtubules as robust SERS substrates based on roll-up nanotechnology. As an illustration, dramatic enhancement is achieved using Rhodamine 6G as a molecular probe, which indicates that a larger plasmonic density of states exist, leading to a greatly enhanced local electromagnetic field (EM) when the sample is irradiated with a laser beam. Optimized results are obtained by controlling the thickness of alumina coating onto Ag-SiO_x microtubes using atomic layer deposition. Finite difference time-domain simulations further illustrate the excitation of localized surface plasmon modes by calculating the EM field properties on the surface of Ag-SiO_x microtubes.

It should be noted that the potential of this approach has not yet been fully exploited, as other methods of producing nano- and microtubular structures, such as those published in papers [14–19], have not yet been tested.

The aim of this paper is to study the application characteristics of SERS substrates of Pt(0) microscrolls produced on the nickel surface as a result of galvanic replacement reaction (GRR) between its atoms and anions in H₂PtCl₆ aqueous solution. For the first time in this way, such microscrolls were obtained in the work [20]. It was shown that they exhibit active electrocatalytic properties in the hydrogen evolution reaction during water electrolysis in an alkaline medium. We also note that earlier GRR have already been used to obtain SERS substrates, for example, in the synthesis of Au-Ag nanocomposites [21–23].

2. Experiment

Dihydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·6H₂O, JSC “Aurat”) and Ni foil with a size of 0.5 × 10 × 10.0 mm were used as precursor and a substrate, respectively, to synthesize the Pt(0) nanolayer by GRR. Ni plates were cleaned with acetone by ultrasonic treatment for 30 min and treated according to [24] in hydrochloric acid (HCl, 3 M). Then, the substrates were washed in deionized water and treated for 30 seconds in a solution of a mixture of CH₃COOH, HNO₃ and HCl acids. At this stage, the chemical polishing of the surface took place and the samples acquired a mirror shine. Thereafter, Ni plates were immersed into a solution of H₂PtCl₆ (C = 0.005 M) for 0.5–60 minutes. The GRR was carried out at room temperature and atmospheric pressure. As a result, the Pt(0) nanolayer is formed on the surface and rolls up into microscrolls during drying in air. SEM, TEM, STEM, EDX and HR-TEM methods were used to characterize the samples. SEM analysis was carried out with a Zeiss Merlin or a Zeiss EVO-40EP electron microscopes. TEM, STEM, and HR-TEM micrographs were obtained using a Zeiss Libra 200 microscope. EDX spectra were received with Oxford Instruments INCA 350 and INCAx-act spectrometers, which were equipped with a Zeiss EVO-40EP and Zeiss Libra 200 electron microscopes, respectively. The Raman spectra were recorded using a Bruker spectrometer (Senterra model) under excitation by a 532 nm laser and a power of 20 mW, the radiation focusing area on the sample had a diameter of about 1 mm without using a microscope objective. Alcoholic solutions of Rhodamine 6G of various concentrations were used as the research object which were applied to the surface.

3. Results and discussions

The study of the nickel surface by the SEM and STEM methods (Fig. 1) and by the EDX method (not shown in the figure) after its contact with an H₂PtCl₆ solution made it possible to establish that, at a treatment time of more than 2–3 minutes, Pt(0) nanolayers with a morphology of partially formed microscrolls are observed. With an increase in treated time, the thickness of the walls of such microscrolls increases from 80 nm to about 120 nm for the samples obtained during treatment with a solution of 3 minutes and 20 minutes, respectively (Fig. 1d,e,f). An increase in the treatment time also leads to an increase in the number of such microscrolls per unit area of the substrate surface. It is also noteworthy that the Pt(0) layer is porous and consists of separate nanoparticles. These nanoparticles form agglomerates, which have the form of pointed vertices on the outer side of a layer with respect to the substrate, directed along the normal to the surface. Such peaks up to 100 nm in height can be clearly identified in the sample obtained during 10 min of treatment with an H₂PtCl₆ solution (Fig. 1e). Increasing the treatment time to 20 minutes reduces the number of such vertices/ It is likely due to the fact that the new nanoparticles Pt(0) that are formed during the synthesis process are located between these vertices. It should also be noted that the thickness of the Pt(0) nanolayer is practically not increased by increasing the treatment time in the solution to 60 minutes, indicating that the nickel surface is blocked by the already formed Pt(0) nanolayer.

The study of Pt(0) nanolayer fragments by TEM and STEM methods made it possible to establish that the size of platinum nanocrystals is 5–10 nm, regardless of the treatment time. Each of these particles has a face-centered cubic crystal lattice characteristic of Pt(0). In this regard, we present in Fig. 2 the results of the STEM and HR-TEM study of only one sample obtained by treating Ni with a H₂PtCl₆ solution for 3 minutes.

A series of experiments that were carried out with Ni foil samples and H₂PtCl₆ solutions showed that the Pt(0) nanolayer with the microscroll morphology is relatively strongly retained on the Ni surface. In this regard, such Ni samples can be used as substrates for obtaining Raman spectra of organic compounds under conditions of signal amplification by the surface. To record such spectra, we used Ni foil substrates with Pt(0) nanolayers obtained on their surface by treatment under GRR conditions in an H₂PtCl₆ solution for 3, 10, and 20 minutes. For comparison, similar spectra of this compound deposited on the single-crystal silicon surface were recorded using a similar technique. The obtained Raman spectra of such samples are shown in Fig. 3.

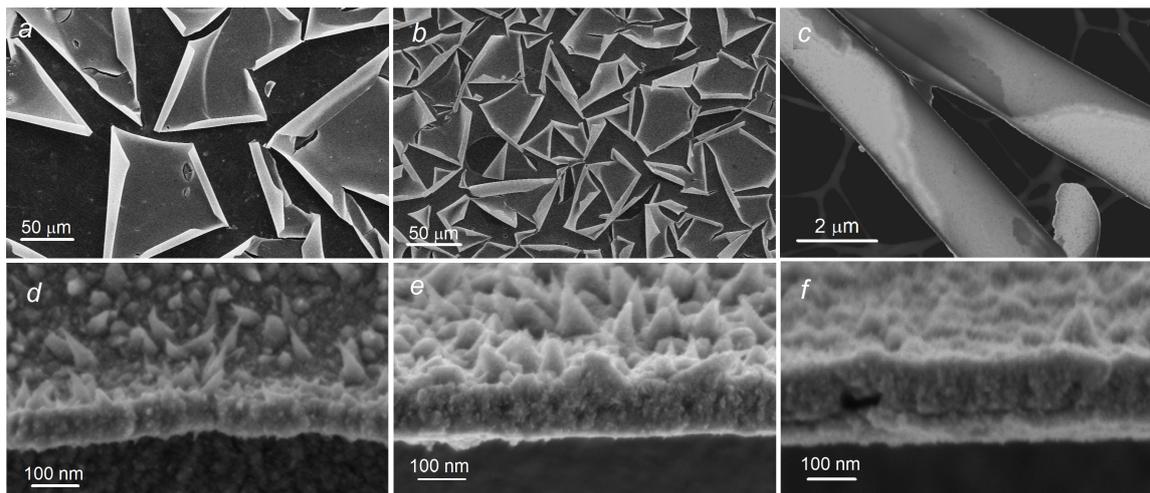


FIG. 1. SEM images of the Pt(0) nanolayers on the Ni surface obtained by treating it for 3 (a,d), 10 (e) and 20 (b,f) minutes with a H_2PtCl_6 solution. (a,b) – general top views, (d,e,f) – side views of the Pt(0) nanolayers. (c) – STEM image of Pt microscrolls obtained after treatment with a solution for 3 minutes

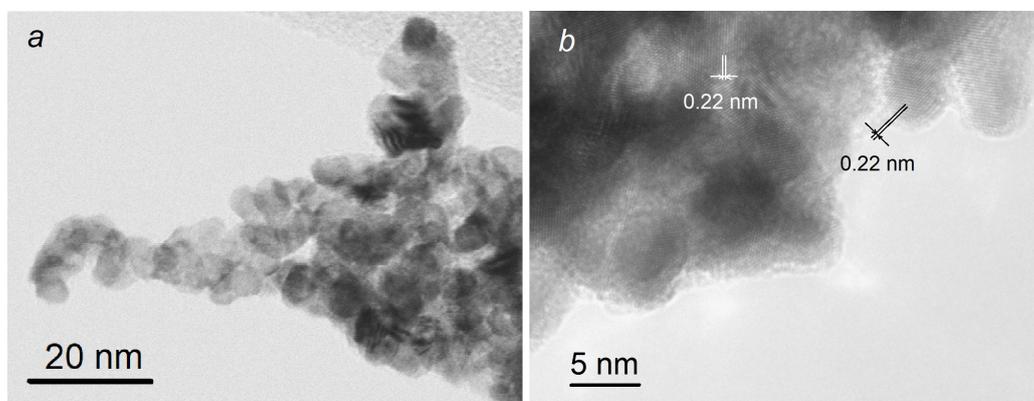


FIG. 2. STEM (a) and HR-TEM (b) images of Pt(0) nanocrystals, obtained after treatment Ni foil with a H_2PtCl_6 solution for 10 minutes

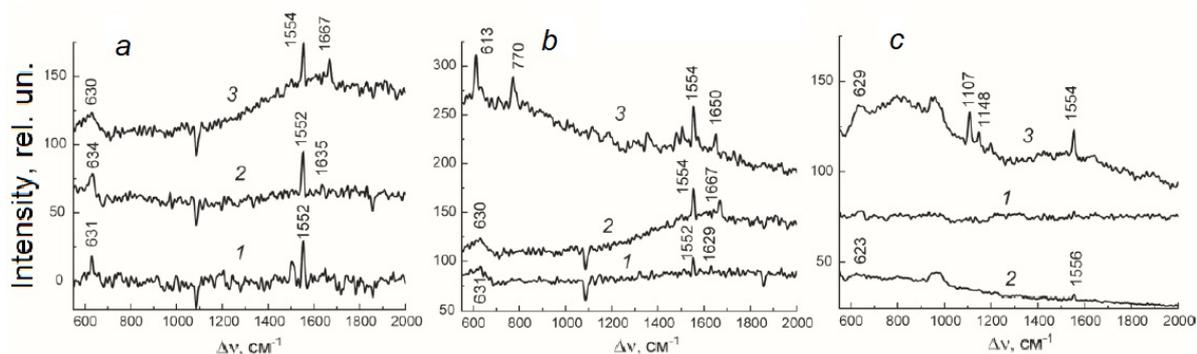


FIG. 3. Raman spectra Rhodamine 6G on the Pt microscrolls surface (a,b) and on single-crystal silicon surface (c) with different concentrations. a – the alcohol solution R6G was applied to the samples prepared under the GRR conditions of Ni treatment with a H_2PtCl_6 solution for 3 (1), 10 (2) and 20 (3) minutes (the concentration of the Rhodamine 6G solution was 10^{-6}M); b – the concentration of Rhodamine 6G solution was 10^{-7} (1), 10^{-6} (2) and 10^{-4} (3) M and it was applied to the sample prepared with a treatment time of Ni with a H_2PtCl_6 solution equal to 20 minutes; c – substrate of the initial silicon (1) and after applying solutions with concentrations 10^{-2} (2) and 10^{-1} M (3)

Analyzing these spectra, first of all, we note that the most informative spectrum of Rhodamine 6G was obtained for the samples prepared by treating nickel in a H_2PtCl_6 solution for 10 and 20 minutes (Fig. 3a(2,3)). In these spectra, in addition to peaks with maxima at 630–634 and 1552–1554 cm^{-1} , one can distinguish peaks with maxima at 1635–1667 cm^{-1} . Recall that the peaks in the region of 1500–1700 cm^{-1} are due to stretching vibrations of C–C atoms in benzene rings, and in the region of 630 cm^{-1} , they are due to vibrations of atoms of chains of C–C–C bonds [25]. Moreover, from the spectra shown in Fig. 3b, it is possible to detect these molecules already in a solution with a concentration of 10^{-7} M. The intensity of the peaks in the Raman spectrum increases with increasing concentration up to 10^{-4} M. In this regard, it can be argued that the detection limit of Rhodamine 6G when obtaining spectra by this method is the value of 10^{-7} M. At the same time, if this solution is applied to the silicon surface, then the most intense peaks in its spectrum are observed only starting from a concentration of 10^{-2} – 10^{-1} M.

Thus, the obtained results indicate that the amplification factor of the studied substrate, which consists of Pt(0) microscrolls on the nickel surface, is 10^5 – 10^6 times. In our opinion, this result is achieved due to the special and unique morphology of the microscrolls layers, the walls of which, on the one hand, consist of nanocrystals with a high specific surface area, and, on the other hand, some of these nanocrystals form arrays of pointed agglomerates. It should also be noted that the walls of microscrolls form a kind of micromirrors for repeated reflection of laser radiation. In our opinion, this may lead to increase of the useful signal. It is also important to note that this effect of increasing the intensity of the bands in the spectrum was achieved using a 532 nm laser, i.e. far from the maximum of plasmon absorption by electrons of Pt(0) nanoparticles, which, as noted, for example, in [26], is at 250–450 nm. In this regard, the proposed substrates for the production of Raman spectra of organic molecules under SERS conditions certainly have great potential for further development. We believe that the creation of nano-composite series based on these samples with other metals, for example with Au and Rh, will make it possible to significantly increase the observed values of the efficiency signal amplification factor. The first experiments on the synthesis of Pt(0) nanocomposites with Rh(0) nanoparticles indicate the possibility of such synthesis.

4. Conclusion

The treatment of chemically polished nickel in a H_2PtCl_6 solution with a concentration of 0.005 M for 2 or more minutes leads to the formation of porous Pt(0) nanolayers with a thickness that depends on the treatment time. These nanolayers are formed by Pt(0) nanocrystals 5–10 nm in size, which, on the outer side with respect to the substrate, form arrays of pointed agglomerates directed along the normal to the surface. After drying in air, cracking of the Pt(0) nanolayers and the formation of partially rolled microscrolls on the nickel surface are observed. Their number is the largest for the samples obtained with a longer treatment time. The features of the practical application of these samples as SERS substrates are studied using the Raman spectra of Rodamin 6G as an example. It is shown that the amplification factor is about 10^5 – 10^6 using 532 nm laser excitation.

References

- [1] Gong T., Das C.M., Yin M.-J., Lv T.-R., Singh N.M., Soehartono A.M., Singh G., An Q.-F., Yong K.-T. Development of SERS tags for human diseases screening and detection. *Coordination Chemistry Reviews*, 2022, **470**, P. 214711.
- [2] Yin Z., Li Y., Xu J., Qian Z.F., Xiong K. Recent advances of perovskite materials for surface enhanced Raman scattering and their applications. *Materials Today Physics*, 2022, **27**, P. 100815.
- [3] Liu C., Xu D., Dong X., Huang Q. A review: Research progress of SERS-based sensors for agricultural applications. *Trends in Food Science and Technology*, 2022, **128**, P. 90–101.
- [4] Povolotckaia A., Pankin D., Petrov Y., Vasileva A., Kolesnikov I., Sarau G., Christiansen S., Leuchs G., Manshina A. Plasmonic carbon nanohybrids from laser-induced deposition: controlled synthesis and SERS properties. *Journal of Materials Science*, 2019, **54**(11), P. 8177–8186.
- [5] Samodelova M.V., Kapitanova O.O., Evdokimov P.V., Eremina O.E., Goodilin E.A., Veselova I.A. Plasmonic features of free-standing chitosan nanocomposite film with silver and graphene oxide for SERS applications. *Nanotechnology*, 2022, **33**(33), P. 335501.
- [6] Eremina O.E., Sergeeva E.A., Ferree M.V., Shekhovtsova T.N., Goodilin E.A., Veselova I.A. Dual-purpose SERS sensor for selective determination of polycyclic aromatic compounds via electron donor-acceptor traps. *ACS Sensors*, 2021, **6**(3), P. 1057–1066.
- [7] Semenova A.A., Veselova I.A., Brazhe N.A., Shevelkov A.V., Goodilin E.A. Soft chemistry of pure silver as unique plasmonic metal of the Periodic Table of Elements. *Pure and Applied Chemistry*, 2020, **92**(7), P. 1007–1028.
- [8] Eremina O.E., Kapitanova O.O., Goodilin E.A., Veselova I.A. Silver-chitosan nanocomposite as a plasmonic platform for SERS sensing of polycyclic aromatic sulfur heterocycles in oil fuel. *Nanotechnology*, 2020, **31**(22), P. 225503.
- [9] Ye J., Jiang J., Zhao Y.S., Yao J. Nano- and microstructured gold tubes for surface-enhanced Raman scattering by vapor-induced strain of thin films. *Journal of Materials Chemistry A*, 2012, **22**, P. 19202.
- [10] Wang X., Wang Q., Chai Z., Mao G., Liu H., Ren X. Gold nanoparticle-induced diameter reduction and enhanced Raman shift in self-rolled-up InGaAs/GaAs microtubes. *Nanophotonics and Micro/Nano Optics III*, 2016, **10027**, P. 100270N.
- [11] Pal U., Castillo López D. N., Carcaño-Montiel M. G., López-Reyes L., Díaz-Núñez P., Peña-Rodríguez O. Nanoparticle-assembled gold microtubes built on fungi templates for SERS-based molecular sensing. *ACS Applied Nano Materials*, 2019, **2**(4), P. 2533–2541.
- [12] Perales-Rondon J.V., Colina A., González M.C., Escarpa A., Roughened silver microtubes for reproducible and quantitative SERS using a template-assisted electrosynthesis approach. *Applied Materials Today*, 2020, **20**, P. 100710.
- [13] Zhang Y., Han D., Du D. Rolled-up Ag-SiO_x hyperbolic metamaterials for surface-enhanced Raman scattering. *Plasmonics*, 2015, **10**, P. 949–954.
- [14] Zhang Z., Tian Z., Mei Y., Di Z. Shaping and structuring 2D materials via kirigami and origami. *Materials Science and Engineering: R: Reports*, 2021, **145**, P. 100621.

- [15] Khalisov M.M., Lebedev V.A., Poluboyarinov A.S., Garshev A.V., Khrapova E.K., Krasilin A.A., Ankudinov A.V. Young's modulus of phyllosilicate nanoscrolls measured by the AFM and by the in-situ TEM indentation. *Nanosystems: physics, chemistry, mathematics*, 2021, **12**(1), P. 118–127.
- [16] Levin A., Khrapova E., Kozlov D., Krasilin A., Gusarov V. Structure refinement, microstrains and crystallite sizes of Mg-Ni-phyllosilicate nanoscroll powders. *Journal of Applied Crystallography*, 2022, **55**(3), P. 484–502.
- [17] Krasilin A.A., Gusarov V.V. Energy model of bilayer nanoplate scrolling: Formation of chrysotile nanoscroll. *Russian Journal of General Chemistry*, 2015, **85**, P. 2238–2241.
- [18] Tolstoy V.P., Gulina L.B. New way of As₂S₃ microtubules preparation by roll up thin films synthesized at the air-solution interface. *Journal of Nano- and Electronic Physics*, 2013, **5**(1), P. 01003.
- [19] Gulina L.B., Tolstoy V.P., Solovov A.A., Gurenko V.E., Huang G., Mei Y. Gas-solution interface technique as a simple method to produce inorganic microtubes with scroll morphology. *Progress in Natural Science: Materials International*, 2020, **30**(3), P. 279–288.
- [20] Kaneva M.V., Tolstoy V.P. The “rolling up” effect of platinum layer obtained on nickel surface by interaction with solution of H₂PtCl₆ and its electrocatalytic properties in hydrogen evolution reaction during water electrolysis in alkaline medium. *Nanosystems: Physics, Chemistry, Mathematics*, 2021, **12**(5), P. 630–633.
- [21] Yang C.-P., Fang S.-U., Tsai H.-Y., Chen J.-W., Liu Y.-C. Newly prepared surface-enhanced Raman scattering-active substrates for sensing pesticides. *Journal of Electroanalytical Chemistry*, 2020, **861**, P. 113965.
- [22] Navarro-Segura M.E., Rivera-Rangel R.D., Arizmendi-Morquecho A., López I., Alvarez-Quintana J., Sanchez-Dominguez M. Ultra-high Sensitivity Surface-Enhanced Raman Spectroscopy (SERS) Substrates Based on Au Nanostructured Hollow Octahedra. *Applied Materials Today*, 2022, **29**, P. 101598.
- [23] Jiang Z., Li C., Liu Y., Jing Q., Liang A. A sensitive Galvanic replacement reaction-SERS method for Au(III) with Victoria blue B molecular probes in silver nanosol substrate. *Sensors and Actuators, B: Chemical*, 2017, **251**, P. 404–409.
- [24] Kaneva M.V., Reveguk A.A., Tolstoy V.P. SILD-preparation of nanostructured Ru_x⁰-RuO₂-nH₂O thin films: Effect of deposition cycles on electrocatalytic properties. *Ceramics International*, 2022, **48**(8), P. 11672–11677.
- [25] Kirubha E., Palanisamy P.K. Green synthesis, characterization of Au–Ag core–shell nanoparticles using gripe water and their applications in nonlinear optics and surface enhanced Raman studies. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2014, **5**, P. 045006.
- [26] Bigall N.C., Härtling T., Klose M., Simon P., Eng L.M., Eychemüller A. Monodisperse platinum nanospheres with adjustable diameters from 10 to 100 nm: synthesis and distinct optical properties. *Nano Letters*, 2008, **8**, P. 4588–4592.

Submitted 9 September 2022; accepted 12 September 2022

Information about the authors:

Maria V. Kaneva – Institute of Chemistry, Saint Petersburg State University, 26 University Prosp, St. Peterhof, Saint Petersburg, 198504, Russia; skt94@bk.ru

Evgen V. Borisov – Institute of Chemistry, Saint Petersburg State University, 26 University Prosp, St. Peterhof, Saint Petersburg, 198504, Russia; eugene.borisov@spbu.ru

Valeri P. Tolstoy – Institute of Chemistry, Saint Petersburg State University, 26 University Prosp, St. Peterhof, Saint Petersburg, 198504, Russia; v.tolstoy@spbu.ru

Conflict of interest: the authors declare no conflict of interest.