= NANOSTRUCTURES = AND NANOTUBES

Morphology and Stability of Composite Silicon–Silver Nanoparticles Produced by Laser Ablation in a Liquid

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Abstract—The possibility of the liquid-phase laser synthesis of silver-decorated silicon nanoparticles with an average diameter of about 120 nm, a diameter dispersion of less than 40 nm, and a size of decorating Ag nanoclusters in the range from 5 to 15 nm is shown as a result of the picosecond laser ablation of silicon targets in a water-ethanol solution containing dissolved silver nitrate (AgNO₃) crystals. At a fixed laser pulses exposure time, the morphology of the nanoparticles depends on the ratio of water and ethanol in the solution and the concentration of silver nitrate. It is demonstrated that the pH factor of the buffer medium has a direct influence on the stability and decorative coating properties of the produced nanoparticles.

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INTRODUCTION

Silicon nanostructures produced by modern nanotechnology methods, due to their unique optical and electrophysical properties, are widely used in microelectronics [1-3], nonlinear optics [4], and plasmonics [5]. Of particular interest are silicon nanoparticles (SiNPs), which can be used in biophotonics applications for the therapy and theranostics of various diseases [6, 7], since suspensions with concentrations of these particles of no more than 0.1 mg/mL are characterized by low toxicity [8], high biocompatibility [9] and, under certain conditions, biodegradability within a few hours [10].

Today, significant progress has been achieved in the application of SiNPs as fluorescent markers for imaging biological systems [11-13] and contrast agents in optical coherence tomography [13-15]. Also, recently the structural and optical properties of SiNPs have been actively studied in connection with a rapidly developing area of cancer treatment: tumor photohyperthermia [16-18]. Research in this area has revealed a significant limitation in the effective use of SiNPs associated with the relatively low absorption of optical radiation by silicon in the wavelength range above 700 nm, where most biological tissues are transparent. Therefore, with an increase in the wavelength of radiation and, accordingly, the depth of its penetration into the body, it is necessary to increase the concentration of SiNPs, which is undesirable from the point of view of nanosafety and the requirement for the rapid biodegradability of therapeutic nanoagents.

The functional capabilities of SiNPs can be expanded by partial (core—satellite-type system) or complete (core—shell-type system) coating of their surfaces with nanoinclusions of noble metals (Ag, Au, etc.), so-called decoration. As a result, composite nanomaterials are synthesized that combine the properties of both a semiconductor with a high refractive index and low optical losses, and a metal that promotes the increased heating of nanoparticles due to plasmonic absorption [4, 19–23].

It should be noted that not only for biophotonics, but also for other areas, the combination of semiconductor and plasmonic concepts within the framework of composite nanomaterials is considered as a step towards the design of completely new nanostructures with improved functionality for solving specific problems in the relevant areas [4, 5, 19–23]. Part of this work aims at the production and study of the properties of SiNPs decorated with gold (Si/Au). Composite Si/Au nanoparticles (NPs), besides the potential for use as photothermal converters of optical radiation [19–21], can be characterized by an enhanced nonlinear optical [4] or magneto-optical [23] response, which expands the range of their application as optical switches and sensors. Silicon-silver (Si/Ag) nanostructures are also characterized by a pronounced plasmonic response [5, 22] and can be successfully used in biomedical applications. However, to date, Si/Ag NPs have been generally less studied from this point of view than Si/Au NPs.

The main issues of the synthesis of functional Si/Ag nanocomposite particles for use in living organisms arise from the need to simultaneously satisfy the following requirements:

(i) control and monitoring of NP sizes during the synthesis process;

(ii) chemical purity of the formed structures and the absence of undesirable toxic inclusions;

(iii) chemical stability of the formed NPs with a silver coating in media with varying acidity, corresponding to the pH factor of real parts of a living organism.

The first requirement follows both from the need to introduce small-sized particles (about 100 nm or less) into living organisms or to apply them to the surface, and from the influence of the size of the decorating structures on the position and width of the plasmon peak. The second and third requirements are respectively related to biocompatibility and preservation of the functional properties of NPs when solving diagnostic and therapeutic problems.

There are several ways of partially satisfying these requirements with the help of chemical technologies known at present. In particular, it is quite simple to form arrays of silicon nanowires using metal-assisted chemical etching and decorate their tips with both silver and gold NPs from solutions of the corresponding salts [24, 25]. However, in this case, such structures are not individual NPs, but are rigidly connected to the initial silicon substrate and are not intended to be introduced into the organs of living organisms. Such composite nanosystems are used as sensors of deposited pathogenic bacteria with increased sensitivity due to the presence of a decorative coating and the effect of giant Raman scattering.

Colloidal Si/Ag core-shell composites can be formed as a result of galvanic reactions using the galvanic-displacement coating technology, but in this case, NPs are predominantly obtained in the form of flakes on the order of several hundred nanometers in size [26], which complicates the further introduction of such fairly large agents with "sharp edges" into living organisms.

It should be noted that physical methods, unlike chemical ones, allow the creation of smooth-shaped composite NPs in a dispersed phase with a size of less than 100 nm. Examples include the production of core—satellite-type Si/Ag NPs using heterogeneous gas-phase synthesis with the simultaneous magnetron sputtering of silicon and silver targets [27] and Ag/Si structures with a silver core and silicon shell using the method of evaporation of these substances with a relativistic electron beam followed by condensation of the vapors in an argon flow [28]. The disadvantages of these approaches include considerable complexity of their implementation, which affects the further scaling and commercialization of the corresponding technologies; as well as the formation of silicon components predominantly in the amorphous phase, which limits the potential areas of application of the formed NPs, for example, for the fluorescent imaging of biological tissues.

To a large extent, the technology of pulsed laser ablation (liquid-phase laser synthesis) is free from the listed disadvantages. It opens up extensive possibilities for the fabrication of silicon-based NPs, including decorated SiNPs (DSiNPs). In the latter case, such structures can be formed as a result of the ablation of silicon and decorating metal in liquid [19–21] or by the ablation of silicon in solutions containing salts or acids of the corresponding metal [4, 5, 29].

An important advantage of the laser ablation method is that when using powerful laser pulses, particles are formed without undesirable toxic impurities, i.e., so-called green synthesis is implemented [7].

In previously published papers on the liquid-phase laser synthesis of SiNPs, it was noted that varying the parameters of laser radiation, buffer media, and types of irradiated targets allows controlling their size distribution, degree of crystallinity, and yield of the ablation products [13, 14, 30].

However, existing works on the formation of Si/Ag type DSiNPs by laser ablation only show their potential for use in biomedical applications [5, 22] without a detailed analysis of the morphology of the formed nanocomposite structures depending on the manufacturing parameters and the stability of the NPs in media with varying acidity, which correspond to different systems of living organisms. These studies also seem relevant given the importance of studying the safety of using silver NPs in real biological systems [31].

In this paper, we investigate the formation and morphology of Si/Ag DSiNPs obtained using a singlestep laser irradiation technology on a single-crystal silicon wafer in a water—ethanol solution containing dissolved AgNO₃ crystals at different ratios of water and ethanol and concentrations of the specified silver salt. The stability of the formed colloidal solutions of DSiNPs in liquid media with varying acidity (pH factor) is studied.

MATERIALS AND METHODS

Suspensions of Si/Ag nanocomposite particles were prepared by the picosecond laser ablation of a *p*-type single-crystal silicon wafer with the (110) surface orientation and a specific resistivity of $\rho = 1-20 \Omega$ cm. Ablation was carried out in water—ethanol solutions. Distilled deionized water obtained using a Milli-Q Integral 15 system (Germany) and 96% commercial ethanol were used to prepare the solution. The listed liquids were mixed in various proportions (Table 1).

Table 1. Parameters for the fabrication of Si/Ag DSiNP samples by laser ablation of a silicon target in solution with different water—ethanol ratios and AgNO₃ salt concentrations

Sample	Water : ethanol ratio in the solution	Concentration of AgNO ₃ , mol/mL
1	1:1	5×10^{-6}
2	9:1	"
3	1:9	"
4	"	10^{-5}
5	"	5×10^{-5}
6	"	10^{-4}
7	"	0

AgNO₃ crystals (purity level 99.9%, ZAO Bertuz) were dissolved in the water—ethanol solution as a precursor of silver NPs. To change the morphology of SiNP decoration during the experiments, the initial molar concentration of AgNO₃ in solution (Table 1) was additionally varied. The choice of water and ethanol as components of the solution is due to the possibility of dissolving AgNO₃ crystals in water, and ethanol, in turn, acts as a surfactant, which ensures the decoration process [5].

Also for comparison, a SiNP sample without decoration was prepared by laser ablation in a water—ethanol solution containing no $AgNO_3$ crystals (sample 7 in Table 1).

Ablation was performed in a glass cuvette with a round bottom and an area of 10 cm^2 . A silicon wafer with a thickness of 470 µm was placed at the bottom of the cuvette so that the solution layer above it was ~3 mm, which, on the one hand, ensured constant coverage of the target with liquid during the ablation process, regardless of the evaporation and cavitation processes occurring under laser irradiation, and on the other hand, the absence of the significant absorption of laser radiation in a relatively thin layer of liquid.

Irradiation was carried out using an EKSPLA PL2143A (Lithuania) picosecond laser with a Nd:YAG crystal: wavelength of 1064 nm, pulse duration and energy of 34 ps and 10 mJ, respectively, and pulse repetition frequency of 10 Hz. The radiation was focused onto the sample by a lens with a focal length of F = 40 mm at normal incidence. In all experiments, the exposure time to laser pulses was fixed and equal to 60 min. The laser pulse fluence was 14.0 J/cm² and significantly exceeded the ablation thershold of single-crystal silicon in water and ethanol [32].

To prevent degeneration of the silicon target during the ablation process, the cuvette was moved in the scanning mode in the horizontal plane using a system of two orthogonal mechanical translators Standa (Lithuania) controlled by a personal computer.

After preparation, the DSiNP samples (samples 1– 6 in Table 1) were centrifuged using an Eppendorf Centrifuge 5424 (Germany) for 8 min at a rotation speed of 14000 rpm to remove residual fragments of AgNO₃ salts. Next, the water–ethanol solution for all samples was replaced with distilled deionized water and the samples were homogenized in an ultrasonic bath for 10 min.

To study the structural properties and morphology of the formed NPs, droplets of the obtained suspensions were deposited onto silicon substrates. After drying, the particles on the substrates were analyzed by scanning electron microscopy (SEM) using a Carl Zeiss Supra 40 electron microscope (Germany). Histograms of the particle-size distribution were constructed by analyzing SEM images. To construct each histogram, we analyzed 200–400 particles.

The chemical composition of the fabricated Si/Ag nanocomposite particles was analyzed by energy-dispersive X-ray spectroscopy (EDX). Measurements of the DSiNPs deposited from the suspension onto GaAs substrates were carried out using a MIRA TESCAN (Czech Republic) scanning electron microscope with a built-in AZTEC ONE module.

The influence of the pH of the buffer medium on the morphology and stability of Si/Ag DSiNPs was studied in distilled deionized water, acetic acid CH₃COOH, and 10% aqueous solution of ammonia NH₄OH. The pH values were determined using a Thermo Orion 410A pH meter (USA). The DSiNP suspensions were immediately centrifuged at 14000 rpm for 10 min after preparation and then placed in cuvettes with the indicated liquids. After 24 h, the suspensions were centrifuged again for 8 min, and the original buffer medium was replaced with water.

The stability of the prepared DSiNP suspensions was assessed based on analysis of the electrokinetic potential values (ζ potential) obtained using a Malvern NANO-ZS dynamic light scattering (DLS) analyzer (England).

RESULTS AND DISCUSSION

According to the SEM data, all Si/Ag nanocomposite particles are fairly smooth and have a shape close to spherical. A typical image of the DSiNPs is shown in Fig. 1a. The morphology of such DSiNPs corresponds to a core-satellite type system, since the surface of the SiNPs is decorated predominantly with isolated Ag nanoclusters of arbitrary shape and sizes in the range from 5 to 15 nm. The silicon cores are an



Fig. 1. SEM images of NPs fabricated by laser ablation of a silicon target in solutions with a water to ethanol ratio of 1:9 and the content of AgNO₃ salts with concentrations of 5×10^{-6} (a) and 0 mol/mL (b).

order of magnitude larger in size and, based on SEM image analysis, are characterized by a polydisperse size distribution, the analysis of which is presented below.

The formation of DSiNPs may be caused by the processes described in previous works on the formation of Si/Ag nanocomposites. As a result of exposure to powerful laser radiation and corresponding intense heating, the combined formation of Ag nanoclusters occurs through the photochemical laser reduction of AgNO₃ to the phase of metallic silver in liquid solution [22] and SiNPs as ablation products of the silicon target. These SiNPs were in a molten state for some time due to the heating of silicon above the melting point of this material $T_m = 1687$ K and in subsequent processes of cooling and crystallization in the buffer solution acquired an energetically favorable shape, close to spherical. In turn, the decoration process is associated with the fact that as the SiNPs were formed in the



Fig. 2. EDX spectrum of Si/Ag DSiNPs prepared by laser ablation of a silicon target in solutions with water to ethanol ratio of 1 : 9 and the content of AgNO₃ salts with a concentration of 10^{-5} mol/mL.

NANOBIOTECHNOLOGY REPORTS Vol. 19 Suppl. 1 2024

solution, these particles locally absorbed the energy of laser pulses, which led to continuous heating of the surface areas where the predominant growth of Ag nanoclusters occurred [5].

Comparison of SEM images of DSiNPs (Fig. 1a) and SiNPs without the addition of $AgNO_3$ into the solution (Fig. 1b) formed in this work under the same technological parameters revealed that the decoration process occurring during the action of laser pulses on the surface of Si particles with Ag nanoinclusions does not affect the smoothness and does not mechanically deform the shape of the silicon particles. In this way, the liquid-phase laser synthesis of DSiNPs is implemented, characterized by a smooth shape and spherical symmetry, which should facilitate the safe introduction of such nanocomposite particles into biological tissues with minimal damage.

The EDX data confirm that the DSiNPs are composed of silicon and silver. Figure 2 shows the typical X-ray spectrum of a DSiNP, which contains lines characteristic of Si and Ag. The spectrum also contains a line related to O, which may indicate a natural oxidation process of the SiNP surface during laser irradiation in liquid. The As and Ga lines refer to the substrate on which the measurements were done.

To study the dependence of the DSiNP morphology on the formation modes, samples were prepared at three different water to ethanol ratios in solution, equal to 1: 1, 9: 1, and 1: 9, and a fixed concentration of AgNO₃ (samples 1–3 in Table 1). The typical SEM images of suspensions of nanocomposite particles prepared in solutions with 1: 1 and 9: 1, are presented in Fig. 3.

In the case of an equal ratio of water and ethanol in the buffer liquid (1 : 1) it is evident that in addition to the process of decorating the SiNP surfaces with silver nanoclusters, individual smooth Ag NPs of arbitrary shape are present in the solution (Fig. 3a). With a



Fig. 3. SEM images of Si/Ag DSiNPs fabricated by laser ablation of a silicon target in solutions with water to ethanol ratios of 1 : 1 (a), 9 : 1 (b) and the content of AgNO₃ salts with a concentration of 5×10^{-6} mol/mL.

ninefold predominance of water over ethanol in the solution (9:1) the decoration process is even less pronounced compared to the increase in the yield of individual Ag NPs in the liquid (Fig. 3b). This is because increasing the water content in the buffer solution improves the solubility of AgNO₃, which leads to the excessive formation of silver fragments in the liquid, which are exposed to high-intensity laser pulses. As a result of the agglomeration of laser fragmentation products, a large number of individual Ag NPs are formed. In parallel with this, a decrease in the content of ethanol, which acts as a surfactant, reduces the efficiency of SiNP surface decoration with the resulting Ag nanoclusters. The optimal result of Si cores decoration with isolated small-sized Ag inclusions, forming DSiNPs with a core-satellite type structure in the experiments, was achieved with a ninefold predominance of ethanol over water in the buffer solution (1:9), as shown in Fig. 1a.

For a detailed analysis of the influence of the parameters of the applied laser technology on the morphology of DSiNPs at the optimal concentration of water to ethanol 1:9, samples were prepared at concentrations of AgNO₃ salts in suspension in the range from 5×10^{-6} up to 10^{-4} mol/mL (samples 3–6 in Table 1). Figure 4 shows SEM images of the NPs prepared at AgNO₃ crystal concentrations from 10^{-5} up to 10^{-4} mol/mL. The corresponding image for the lowest concentration is 5×10^{-6} mol/mL is shown in Fig. 1a.

In case of the lowest content of $AgNO_3$ salts in the buffer liquid (Fig. 1a), Ag nanoclusters isolated from each other partially cover the SiNP surface. As mentioned earlier, the formation of DSiNPs with core-satellite type geometry is observed. Increasing the concentration by 2 times (Fig. 4a) leads to the formation of excess Ag fragments in the melt as a result of heating by laser radiation, followed by aggregation into clusters with larger sizes and arbitrary shapes on the surface of Si cores, as well as to the appearance of individual spherical Ag NPs in the solution, which is associated with the laser fragmentation of excess silver products in the liquid. The hypothesis is confirmed by the fact that a further increase in the concentration of AgNO₃ crystals by 5 and 10 times (Figs. 4b and 4c) stimulates the formation of fairly large Ag NPs in a water-ethanol solution without any preferential decoration of the SiNP surfaces with Ag nanoclusters. As seen in Figs. 4b and 4c the obtained colloidal solutions contained predominantly separate Si and Ag NPs with a smooth spherical shape and approximately similar sizes, which is consistent with the results of work [5], in which a similar tendency of the separation of Si clusters from SiNPs with increasing concentration of AgNO₃ salts was revealed.

Thus, the morphology of Si/Ag nanocomposite particles clearly depends on the ratio of water and ethanol in the solution and the concentration of AgNO₃ crystals. Optimal decoration during the formation of DSiNPs with core-satellite type geometry (Fig. 1a) occurs at optimal process parameters corresponding to a water to ethanol ratio of 1:9 in solution and the lowest initial AgNO₃ salt concentration of 5×10^{-6} mol/mL in the suspension. A further reduction in the AgNO₃ crystal content seemed impractical in the experiments conducted, since it would lead to a decrease in the number of decorated SiNPs.

To determine the average sizes, histograms of the size distributions of DSiNPs (sample 3) produced with optimal synthesis parameters and undecorated SiNPs (sample 7) formed with the same parameters but without the addition of $AgNO_3$ into the solution were constructed by SEM image analysis (Fig. 5). It can be seen that both analyzed NPs suspensions are characterized by polydisperse distributions.



Fig. 4. SEM images of Si/Ag DSiNPs fabricated by laser ablation of a silicon target in solutions with a water to ethanol ratio of 1 : 9 and the content of AgNO₃ salts with concentrations of 10^{-5} (a), 5×10^{-5} (b), and 10^{-4} mol/mL (c).

Utilizing the optimal technological parameters of synthesis in the laser ablation method allows the production of DSiNPs with an average size of 120 nm (Fig. 5a, Table 2). Comparison of the DSiNP size distribution with the undecorated SiNP size distribution (Fig. 5b) revealed no significant differences in the mean sizes and standard deviations (Table 2). Moreover, the values of the latter (size dispersion) do not

NANOBIOTECHNOLOGY REPORTS Vol. 19 Suppl. 1 2024

exceed 40 nm, which is a good result for the pulsed laser ablation method, which, as a rule, allows the creation of SiNPs and DSiNPs with a clearly expressed polydisperse size distribution [5–7]. Thus, the process of decorating SiNP surfaces with Ag nanoclusters has virtually no effect on the size of the formed DSiNPs.

To study the effect of the pH factor of the buffer medium on the morphology and stability of Si/Ag nanocomposite particles, the suspensions were placed immediately, after production, for 24 h in neutral, acidic, and alkaline media, simulating, by choosing the pH factors listed below, the presence of the studied DSiNPs in the systems of real living organisms, such as near-neutral saliva; acidic systems of the esophagus, stomach, and urine; as well as alkaline systems: intestines and blood (arterial, venous, and capillary). The selected buffer solutions included: distilled deionized water as the neutral medium, acetic acid CH₃COOH as the acidic medium, and for the alkaline medium, 10% aqueous solution of ammonia NH₄OH was selected. The measured pH values of the liquids used are presented in Table 3.

SEM images of the DSiNP suspensions after 24-h exposure to acetic acid and ammonia are shown in Fig. 6.

Exposure to an acidic medium does not affect the decoration of SiNP surfaces with Ag nanoclusters, unlike exposure to an alkaline liquid, where the SiNP surface is cleared of silver fragments. Most likely, the process of removing decorating Ag nanoinclusions is due to the formation of negatively charged hydroxyl group ions (OH⁻) during the dissociation of ammonium hydroxide in the 10% solution of ammonia in water used according to the chemical reaction [33]:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$
 (1)

The subsequent electrostatic interaction of negative OH^- ions with positive Ag^+ ions leads to removal of the latter from the silicon cores. It should be noted that distilled deionized water did not affect the morphology of the Si/Ag DSiNPs, and the SEM images did not differ significantly from that shown in Fig. 1a. This is due to the absence of dissolved mineral salts, organic matter, and other impurities in the water used, which could interact with Ag ions decorating the surface of SiNPs.

The stability of the DSiNPs was assessed by analysis of the ζ potential values obtained by DLS (Table 3). For comparison, the following were measured: ζ potentials of the SiNPs without decoration, after being in the buffer liquids indicated above.

NPs in neutral distilled deionized water are characterized by negative ζ potential values, the modulus of which exceeds 20 mV. This confirms the moderate sta-



Fig. 5. SEM histograms of the size distributions of NPs produced by laser ablation of a silicon target in solutions with a water to ethanol ratio of 1:9 and the content of AgNO₃ salts with concentrations of 5×10^{-6} (a) and 0 mol/mL (b).



Fig. 6. SEM images of NPs fabricated by laser ablation of a silicon target in a solution with a water to ethanol ratio of 1 : 9 at a concentration of AgNO₃ salts of 5×10^{-6} mol/mL, after 24 h in acetic acid CH₃COOH (a) and 10% solution of ammonia NH₄OH (b).

bility of SiNPs and DSiNPs in the suspensions after production, i.e., relative resistance to agglomeration.

The DSiNPs and SiNPs without decoration in acetic acid are characterized by positive values not exceeding 20 mV. This indicates an emerging instability, i.e., a tendency to form large agglomerates from the studied NPs. This behavior can be explained by the screening of NPs with an initially negative ζ potential

Table 2. Average sizes, standard deviations, and sizes of Ag nanoclusters for NPs fabricated by laser ablation of a silicon target in solutions with a water to ethanol ratio of 1 : 9 at the optimal concentration of AgNO₃ salts (DSiNP, 5×10^{-6} mol/mL) and in their absence (SiNP, 0 mol/mL)

Type NPs	Average size, nm	Standard deviation, nm	Range of Ag nanocluster sizes, nm
Si/Ag DSiNPs	120	39	5-15
SiNP	118	36	0

Table 3. ζ potential values for NP suspensions produced by laser ablation of a silicon target in solutions with a water to ethanol ratio of 1 : 9 at the optimal concentration of AgNO₃ (DSiNPs, 5 × 10⁻⁶ mol/mL) and in their absence (SiNP, 0 mol/mL), in buffer media with different pH values

	pH of the	ζ potential, mV		
Buffer medium	buffer medium	Si/Ag DSiNPs	SiNPs	
Distilled deionized water	7.0 ± 0.2	-21 ± 1	-27 ± 2	
Acetic acid (CH ₃ COOH)	2.8 ± 0.1	18 ± 1	10 ± 1	
10% aqueous solution of ammonia (NH_4OH)	11.3 ± 0.3	-50 ± 3	-57 ± 4	

by positively charged H^+ ions, which are formed as a result of the dissociation of acetic acid CH_3COOH in colloidal solutions [34]:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
. (2)

The ζ potential values of the suspensions of DSiNPs and SiNPs without decoration in an alkaline medium of a 10% solution of ammonia are negative and in absolute value no less than 50 mV, which indicates high stability, and also confirms the above hypothesis about the removal of decorating Ag⁺ nanoinclusions from the silicon cores.

For all the media used, there is a tendency for the value of the ζ potential to increase (in case of negative values of the decrease in absolute value) upon decoration of the SiNP surface with Ag⁺ nanoclusters due to the screening effect.

Thus, the pH factor of the buffer medium has a direct impact on the morphology and stability of the produced Si/Ag nanocomposite particles. Distilled deionized water is the optimal buffer medium in terms of DSiNP stability, whereas their exposure to acetic acid and aqueous ammonia solution causes the agglomeration of SiNPs into larger clusters and removal of the decorating coating, respectively.

CONCLUSIONS

The study demonstrated the possibility of synthesizing Si/Ag DSiNPs with a core-satellite type geometry, characterized by an average size (diameter) of about 120 nm, a size dispersion of less than 40 nm, and sizes of decorating Ag nanoclusters in the range from 5 to 15 nm as a result of the picosecond laser ablation of a single-crystal silicon wafer in a water ethanol solution containing AgNO₃ salts. At a fixed exposure time to laser pulses, the morphology of the formed composite Si/Ag NPs depends on the ratio of water and ethanol in the solution and the initial concentration of AgNO₃ crystals in the suspension. It was found that the optimal decoration of isolated SiNPs with Ag nanoclusters for further use occurs at a water to ethanol ratio of 1 : 9 and an initial concentration of 5×10^{-6} mol/mL of AgNO₃ salts in this solution. The decoration process of SiNP surface with Ag nanoclusters has virtually no effect on the average size of the formed Si/Ag nanocomposite particles.

It has been demonstrated that the pH factor of the buffer medium affects the decoration of SiNP surfaces and changes their ζ potential: when DSiNPs are placed in acidic and alkaline liquids, the absolute value of the ζ potential decreases or increases due to the influence of H⁺ and OH⁻ ions, respectively. In the latter case, the decorating silver nanoinclusions are removed from the silicon cores. The suspensions of Si/Ag DSiNPs in distilled deionized water are characterized by moderate stability and appear to be the most promising for further use in biomedical applications, such as contrast agents in biophotonics and for photohyperthermia.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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