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COMPOSITE SILICATE FILMS WITH GOLD NANOPARTICLES FOR SURFACE-ENHANCED RAMAN SPECTROSCOPY: SYNTHESIS USING NATURAL PRODUCTS

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Hybrid organic–inorganic films containing gold nanoparticles were obtained by the sol–gel method by hydrolytic polycondensation of tetraethoxysilane in aqueous solutions of honey containing $HAuCl_4$ with an acidic catalyst (HCl). The films were examined by absorption and Raman spectroscopy (RS), transmission electron microscopy, and atomic-force scanning microscopy. It was shown that enhancement (3-5 times) of the Raman spectra is observed in the region of gold nanoparticle aggregates, and this predetermines the potential of such materials as supports for surface-enhanced Raman spectroscopy.

***Key words**: gold nanoparticles, composite films, tetraethoxysilane, surface-enhanced Raman spectroscopy, honey.*

The first references to the use of colloidal gold for aesthetic and medical purposes appeared in the first centuries BC in the treatises of Chinese, Arabic, and Indian investigators. The subsequent interest in colloidal gold was due to its use as additives during the production of "ruby" glasses, porcelain painting, silk dyeing, etc., which as is now known was brought about by the excitation of local plasmon resonance in the nanoparticles of the noble metals [1]. In most cases natural components (plant extracts, honey, sugar, and so forth), the priority and effectiveness of which in an historical context are not subject to doubt, were used for the production of the nanoparticles [2, 3].

Traditional contemporary methods for the production of gold nanoparticles are based on the reduction of derivatives of gold trichloride both in solutions and in various matrices, while the reducing agents may also act as stabilizers of the obtained nanoparticles [2]. Here many authors have remarked that the particles formed with the use of spatially extended polymeric matrices (e.g., polysaccharides, etc.), are distinguished by a wide variety of forms and sizes for the metallic particles [4]. Much more rarely used are methods of synthesis of colloidal gold in the presence of natural components [2, 3]. At the same time modern ecological trends predetermine the need for the development of methods of synthesis employing nontoxic and easily utilized components, giving rise to the urgent need to develop methods for the production of nanoparticles of noble metals (NNMs) using natural compounds. Of special interest are methods for the production of NNM-containing composite materials

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from which structures with various geometries for increasing the efficiency of solar cells [5], SERS-active supports [6], catalysts [7], or other applications of nanoplasmonics [1, 8] can be prepared.

The synthesis of organic–inorganic sol–gel media is usually realized by means of hydrolyzing precursors of the tetraethoxysilane (TEOS) type [9]. In order to obtain hybrid compositions the hydrolytic polycondensation of the precursors is conducted in the presence of inorganic dopants, which confer the specified physicochemical characteristics onto the materials that are formed [8, 9]. As a result of such a synthesis the inorganic components are intercalated in the volume of the matrix and form with it strong intermolecular bonds, which eliminates their spontaneous separation or segregation in the matrix layer. By using tetraethoxysilane as film-forming component it is possible also to increase the adhesion of the films to the glass or metal and to produce particularly strong coatings on the basis of silicides and silicon oxides.

A method for the production of NNM-containing composite materials on the basis of tetraethoxysilane, which is converted into a gel by hydrolysis and condensation, was examined in the present work. Components present in honey were used as reducing agent–stabilizers for the production of gold nanoparticles from aqueous solutions of tetrachloroauric acid. In this case the metal phase is formed in the volume of the solution, and this makes it possible to secure a uniform distribution of the NNM. Since the formation of a sol prevents the formation of extended three-dimensional structures the processes of formation of the noble metal nanoparticles under analogous conditions in the absence of the TEOS were studied in order to determine the role of the three-dimensional organization of the honey components in the solution on the growth of the metal nanoparticles.

The solution of honey was produced by dissolving it in distilled water (300 mg/mL). The cloudy solution was then filtered through a filter with a pore size of 200 nm (Chromafil PES-20/25, Macherey-Nagel) to remove the insoluble fragments and large aggregates. The organosilicon sol was obtained by hydrolytic polycondensation of 15 mL of tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS, 98%, Sigma-Aldrich) in aqueous–alcohol solution [10 and 24 mL (95%) respectively]. Hydrochloric acid HCl (37%) was used as catalyst for hydrolysis and subsequent condensation. The obtained solution was mixed with 10 mL of the honey solution, and 10 mL of $HAuCl_4 \cdot 4H_2O$ (0.001 M, Sigma-Aldrich) was added to the obtained mixture drop by drop with constant stirring. One hour after the components were mixed the initially transparent solution became purple due to the appearance of an unsymmetrical absorption band with a maximum in the region of 550 nm. The characteristic absorption spectra of the solution (USB2000 spectrophotometer, Ocean Optics Inc.), recorded at specific intervals after the components were mixed, are shown in Fig. 1. The obtained gel remains stable for at least a few weeks.

The formation of the metallic phase of the metal nanoparticles in the case under consideration (Fig. 1) differs from the processes observed both for low-molecular reducing agents of the sodium citrate type and for the case with the presence of only honey during the synthesis of the nanoparticles. In fact, for systems in which a stage involving aggregation of the nucleation centers (with the use of sodium citrate, etc.) is observed, the initial sharp increase of optical density in the long-wave region (observed as bluing of the system) is replaced by a gradual shift of the absorption maximum from 700 to 520 nm [10]. In the case where only the honey components are used as reducing agent–stabilizer a smooth increase of optical density is observed with absorption maxima at about 550 and 720 nm (data not given). Here the band in the region of 720 nm does not disappear with time but becomes more clearly defined. In the case under consideration one unstructured band is observed in the region of 550 nm, and its intensity increases in the course of time (Fig. 1a). The position of the maximum of this band corresponds closely to the absorption of gold nanoparticles of spherical form [1]. The presence of the unstructured absorption in the region of more than 600 nm indicates the presence of aggregates of the metal nanoparticles, the relative amount of which remains practically unchanged with time [1]. (The form of the band is preserved.)

Analysis of the changes in the absorption spectrum, presented in Fig. 1, makes it possible to single out a series of interesting features of the synthesis of the NNMs in this case. Comparison of the relationships for the relative absorption of the solutions $\Delta D(550)$ at 550 nm (the difference in the optical densities at 550 and 850 nm; the proportional absorption by the gold nanoparticles without regard to scattering) with the relationship for the change of the optical density at 850 nm $D(850)$ (proportional to the scattering of light) makes it possible to identify a series of important features. Thus, for example, for 1 h after the solutions are mixed the scattering of the solutions $D(580)$ increases without change of the absorption $\Delta D(550)$, indicating the formation of three-dimensional structures whose coefficient of refraction differs from the average for the solution. This is confirmed by the increase of the absorption in the region of 300 nm, indicating the formation of organosilicon structures or their complexes with gold. This gives rise to the formation in such a system of spatially restricted regions

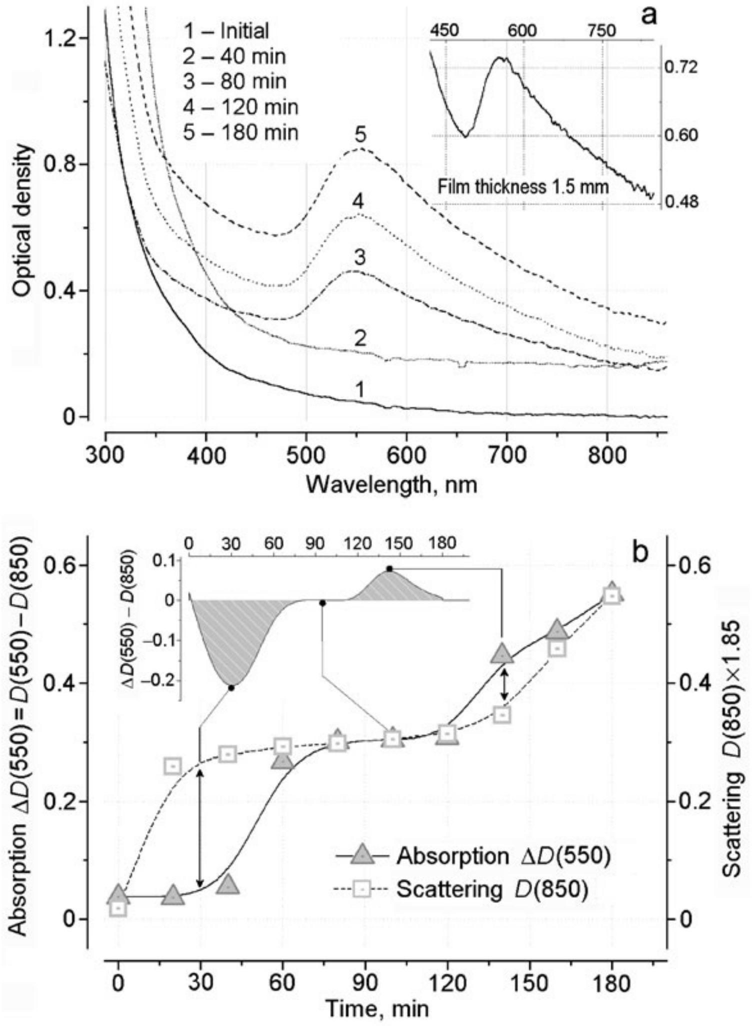

Fig. 1. a) The absorption spectra of the water–alcohol mixture of tetraethoxysilane, hydrochloric acid, and chloroauric acid after addition of the honey solution (inset: the absorption spectrum of a film of thickness 1.5 mm); b) the dependence of the absorption intensity at 550 and 850 nm in the spectra of Fig. a [inset: the difference of the optical densities corresponding to absorption by the metal nanoparticles Δ*D*(550) and scattering of light by the solution *D*(850)].

separated probably by an organosilicon "network" – the nucleation and growth of primary crystals of gold is realized in the cells of such a network.

Subsequent increase of the absorption due to the formation of gold nanoparticles Δ*D*(550) takes place without change of the scattering, indicating that the average size of the formed organosilicon structures is preserved. The further increase of the absorption for 2 h after the beginning of the synthesis is characterized by a simultaneous increase of the absorption and scattering. This makes it possible to suppose that the increase of the absorption is due to increase in the size of the individual nanoparticles of gold and not their number. In this case the NNMs are template agents promoting the formation of silicate or hybrid nanocomposites of specific structure (e.g., nanoparticles of gold coated with a silicate shell). Thus, the data from analysis of the optical spectra make it possible to suppose that the synthesis of the gold nanoparticles in the investigated case goes through a stage of formation of spatially separate small nucleation centers (or their aggregates), some of which

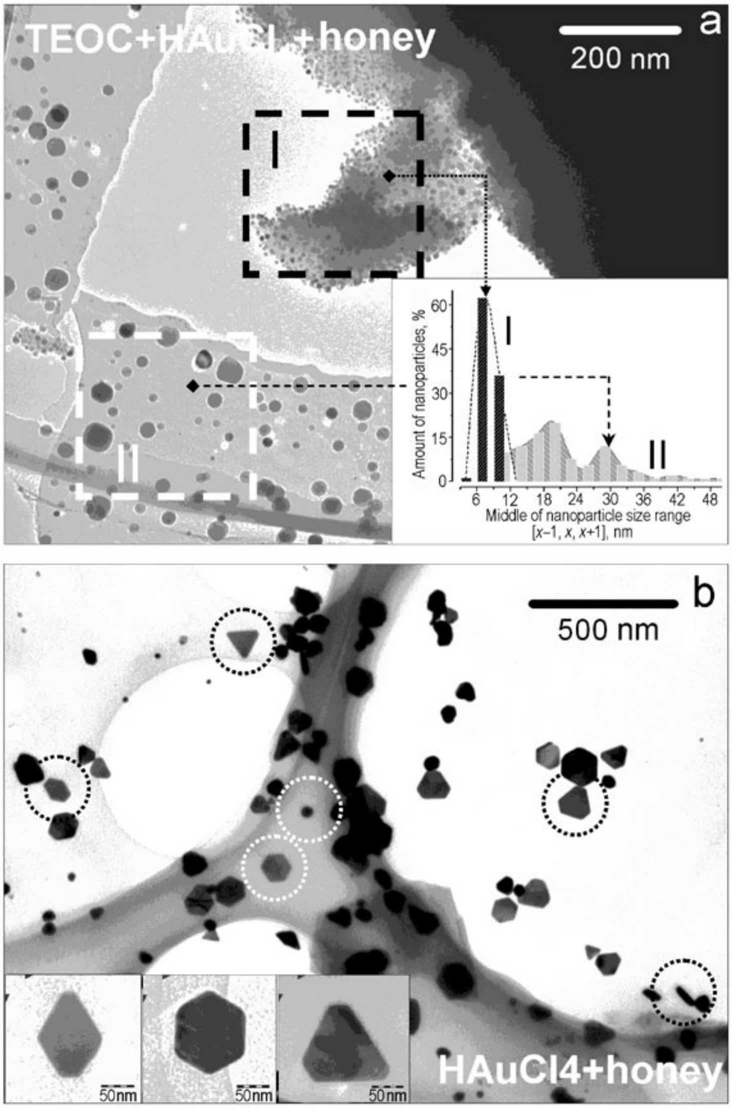

Fig. 2. Images of the gold nanoparticles produced in solutions containing: a) honey, $HAuCl_4$, TEOS [inset: distribution of the particles in regions I (the region of the gel) and II (outside the gel)]; b) honey and $HAuCl_4$ (inset: enlarged images of the characteristic nanoparticles of nonspherical form).

subsequently increase in size. In order to confirm this suggestion investigations with a transmission electron microscope (TEM, JEM JEOL-1011, Japan) were carried out.

As seen from the data presented in Fig. 2a, in the presence of TEOS the gold crystals are formed as spherical particles of various sizes. In the regions of the organosilicon sol particles of 7 ± 1 nm predominate (Fig. 2), whereas outside the sol the size of the particles is significantly larger (right up to 40-50 nm with maximum distribution at 20 ± 1 nm). Filtration through a filter with pores of 200 nm leads to removal of the sol from the solution.

In the absence of TEOS, in addition to the particles of spherical form (with maximum distribution at about 30 nm) particles in the form of regular isosceles triangles, equilateral hexagons, and triangles with symmetrically truncated vertices, due to the face-centered cubic lattice of the gold, are produced (Fig. 2b). Similar structures were observed by other authors using sugars, proteins, polyphenols, carbohydrates, polymers, etc. as reducing agent–stabilizers [2, 3]. Thus, for example, in the case of polymers the formation of the nanoparticles of nonspherical form is due to the geometry of the nanoreactor: the

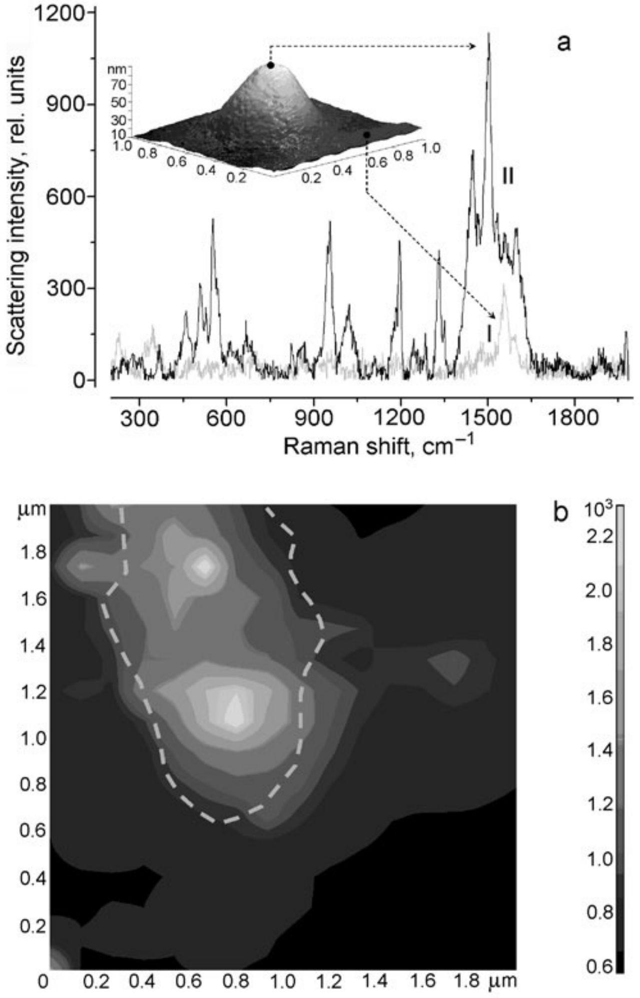

Fig. 3. a) The Raman spectra for the surface aggregates of gold nanoparticles (inset: image of the aggregate of gold nanoparticles, obtained with the use of an atomic-force microscope); b) the distribution of the Raman intensity on the surface of the film in the region of the peak at 1500 cm^{-1}. The dashed line shows the contour of the integral (from the spectrum) Raman intensity.

adsorption of gold ions on the chains in the spatially restricted regions with given distribution of functional groups leads to reduction and subsequent nucleation. The directional growth is due to the predominant adsorption of the side residues of the polymeric chains on certain faces of the nucleation center, as a result of which the metal ions can only diffuse to the end sections of the growing crystal [4]. The motivating force of the anisotropic growth is the difference in the crystal structure of the faces, and as a result the crystal grows along some isolated axis.

The formation of nonspherical particles in a macroscopically isotropic medium containing a low-molecular reducing agent can only arise in the presence of anisotropic phase boundary brought about by a combination of the spatial fluctuations of the density and the mass-transfer processes. The molecules of fructose and glucose, which are the main components of honey (more than 75% [11]), can act as reducing agent–stabilizers during the growth of the particles. As a result of their structural features they are capable of forming spatially organized dynamic supramolecular assemblies leading, for example, to rotation of the plane of polarization of light in their solutions. The metallic phase is formed in the same regions of the solution where dynamic nanoreactors with the necessary arrangement of functional groups for nucleation and stabilization of nanocluster are created as a result of cooperative interaction of the molecular fragments. The aldehyde groups of the glucose molecules act as reducing agent, while the fructose is a stabilizing and shape-forming agent as a result of the presence of a ketone fragment in its structure [11, 12]. The addition of TEOS to the reaction mixture prevents the formation of such three-dimensional structures, and it is this that gives rise to the growth of only spherical nanoparticles of the metal.

The thin-film coatings of hybrid organic–inorganic sols were produced by the deposition of the solution onto the substrate followed by drying at room temperature. Since the absorption of films with a thickness of a few microns was insufficient for quantitative determination of the characteristic bands of the gold nanoparticles as a result of strong scattering, special samples with a thickness of about 1.5 mm were prepared by evaporation of the gel at room temperature. The characteristic absorption spectrum of such samples is shown in the inset of Fig. 1a. In spite of the fairly strong scattering of the films, the absorption characteristic of the gold nanoparticles in the region of 550 nm is observed in the form of a broad asymmetric band similar to that in the solution. It is interesting to note that the absorption characteristics remain practically unchanged in the transition from the solution to the film, irrespective of its thickness. (The absorption spectra of the films with micron and millimeter thicknesses are similar.) This is due to the presence of a silicate network demarcating the space between the nanoparticles and preventing their aggregation.

In order to investigate the possibility of using the obtained films as supports for surface-enhanced Raman spectroscopy the Raman spectra of films (thickness 1-5 μm) inside and outside the regions of the clusters of metal nanoparticles were studied. Since the increased Raman scattering at gold nanoparticles is caused by the excitation of local plasmon resonance, with a laser having an emission wavelength of 632.8 nm excitation of the individual nanoparticles (with an absorption maximum in the region of 550 nm) in the matrix did not occur. The measurements were therefore made on the surface aggregates of particles with an average size in a surface plane of about 100 nm, the spectrum of which contains long-wave absorption in the region of 600-700 nm [1]. Figure 3b shows the results of such measurements using a combined system based on an atomic-force microscope and a Raman spectrometer (NTEGRA Spectra platform, NT-MDT Inc., Russia). In the region outside the gold nanoparticles (with mean-square roughness in the range of 2-7 nm) the intensity of Raman scattering is at the noise level. At the same time in the region of the aggregates of gold nanoparticles there are clearly defined Raman bands corresponding to compounds that are in direct proximity to the metal nanoparticles.

Analysis of the Raman data for the films produced in the absence of honey indicates that the hydrolysis process of the TEOS under the given conditions goes almost to completion – the band at 651 cm^{-1} corresponding to the $\nu_s(Si(OC_2H_5))$ is absent. The formation of the SiO_x matrix is confirmed by the presence of a doublet at 1100 and 1500 cm^{-1} (Si—O—Si) and a maximum at 450 cm^{-1} (SiO_2) [13]. The bands in the Raman spectrum in the region of the nanoparticle aggregates can be assigned to the immobilized molecules of the sugars (874 cm^{-1}, C—H) and particularly glucose (400-519 cm^{-1}), amino acids (1088 cm^{-1}, C—N; 1418 cm^{-1}, C—O—O), hydrocarbons (1196 cm^{-1}, C—OH) and the symmetrical CH_2 vibrations and the deformation OH vibrations in various compounds (1497-1541 and 1632 cm^{-1} respectively) [14, 15]. Figure 3b shows the three-dimensional distribution of the Raman intensity in the region of the most intense Raman band at 1500 cm^{-1}, which indicates a 3-5-fold increase in the region of the aggregates of the metal nanoparticles. As seen from the figure, the size of the region of the intensified Raman spectrum amounts to about 200 nm in diameter, which agrees well with the results from analysis of these sections of the surface using the atomic-force microscope (the inset in Fig. 3a).

The comprehensive investigations of the thin-film composite structures based on silicate matrices with gold nanoparticles intercalated in their volume make it possible to propose them for potential use as functional templates in the creation of supports for procedures based on Raman scattering, plasmon photonics, and nanoelectronics employing natural compounds.

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