

Gold Nanocrystals as a Substrate for Micro Raman Spectroscopy

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(Received 04 September 2011; in final form 23 May 2012; published online 04 June 2012)

The Raman spectra of rhodamine R6G dye molecules in polymethyl methacrylate were investigated by using microraman spectroscopy technique. It was shown that these spectra are enhanced due to the presence of the gold nanocrystals. As the substrates, we used washed from organic overlayer the gold crystals which possess shape of thin nanoprisms with basement of the equilateral triangles, truncated triangles, and hexagons. It was found that the highest intensities of certain Raman peaks are enhanced up to 10^4 times when the Raman signal is excited with laser beam ($\lambda_{ex} = 632,8$ nm) focused on an apex of gold nanoprism. We have discussed the possible mechanisms of the revealed enhancement.

Keywords: Nanocrystals, Gold, Micro Raman spectroscopy, Rhodamine R6G.

PACS numbers: 61.46.Hk, 78.30. – j

1. INTRODUCTION

Raman spectroscopy is a very sensitive and effective investigation method of the macromolecular structure and their conformational changes, and it is also used for identification and determination of small quantities of the substance that is important for pharmacy, ecology, analytical chemistry [1-3], biosensorics [3-5], biomedical diagnostics and nanomedicine [6-9].

Possibilities of the considered method increase if use specially made substrates on which studied substance is deposited. Intensity of the Raman scattering spectra by adsorbed molecules on such surfaces is enhanced up to several orders (the so-called giant Raman scattering (GRS) or surface-enhanced Raman scattering (SERS)). Amplification is conditioned by two mechanisms: the electromagnetic and chemical (molecular) ones [10, 11]. The first mechanism is connected with sharp increase in the local fields in the case of the resonant interaction of the incident light wave with surface plasmons. The second, chemical or adsorption-molecular, mechanism is connected with the interaction of adsorbed substance with metal surface, and as a result, polarizability of adsorbed molecule is increased due to the increase in its dipole moment or because of the formation of metal-adsorbate complex with charge transfer [10, 12].

Gold, silver (more rarely – platinum, palladium, and copper) rough surfaces or nanoporous films [13], as well as nanoparticles of these metals, whose sizes are much less than the light incident wavelength, are the most frequently used as substrates. Excitation of the plasmon resonance is determined by both geometric and optical (dielectric) properties of metal. For metals, real part of the permittivity is negative in the optical wavelength range, and therefore, light decays rapidly in the volume. But on the dielectric-metal interface during interaction of the electromagnetic wave with metal surface, surface plasmons can appear: collective oscillation of sharing electrons which reaching the resonance with electromagnetic incident wave leads to the sharp amplification of

the local (near the surface) field. Such amplification is maximum on the apexes of non-uniformities, the so-called “hot points” (geometric factor).

Why gold or silver? First of all, amplification coefficient, which is directly proportional to the square of the ratio real-to-imaginary part of permittivity, in the optical wavelength range is considerably higher for silver than for gold, since in this range the value of imaginary part of the permittivity is less for silver than for gold [14]. On the other hand, gold is more inert metal in comparison with silver which is easily oxidized. Therefore, gold substrates or nanoparticles are more stable with respect to corrosive media.

Recently, in connection with sharp amplification of electromagnetic field in “hot points”, gold nanoparticles of non-spherical shape in suspension form or deposited on substrate for their usage in SERS spectroscopy [4, 15, 16] are of a great interest. Theoretical calculations of amplification of electromagnetic field depending on the particle shape (including triangular nanoprisms) and their environment are carried out in works [17-20]. However, there are not many experimental works which confirm theoretical calculations [21-23].

In the given work, we have investigated and shown experimentally that synthesized in aqueous and non-aqueous media plane gold nanocrystals of different morphology can be successfully used as a substrate whose surface amplifies Raman scattering by the deposited molecules of analyte.

2. EXPERIMENTAL PART

Aurichlorohydric acid $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich), ethylene glycol (chemically pure, Germany), polyvinylpyrrolidone (29 kDa, Sigma-Aldrich), ethyl alcohol, distilled water, polysaccharides (PS), microalgae *Chlorella vulgaris* LARG-3 were used to synthesize gold crystals. The latter were preliminarily isolated by the technique [24] from culture medium after separation by centrifugation of chlorella cells from suspension. Mean molecu-

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lar weight of PS – 500 kDa – was defined by the high-performance liquid chromatography (HPLC) method [25]. Hexane and acetonitrile were used in individual cases for the formation of gold film on the glass surface.

Gold single crystals in the form of plane nanoprisms of different morphology (equilateral triangles, truncated triangles, and hexagons) were obtained in aqueous and non-aqueous media (Fig. 1).

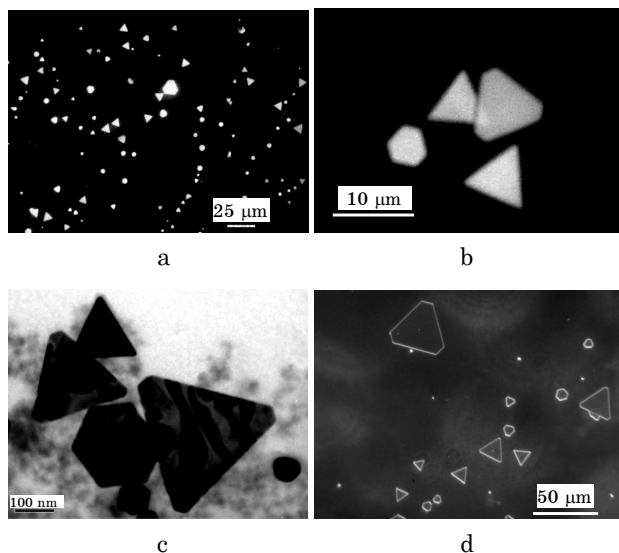


Fig. 1 – Gold crystals synthesized in aqueous (a, b) and non-aqueous (c, d) media. Micrographs are obtained by the methods of electron (c) and optical microscopy in the mode of light (a, b) and dark (d) fields

Technique for producing gold micro- and nano- single crystals in aqueous medium is protected by the patents [26, 27]. Properties of the obtained crystals, morphology, kinetics, growth mechanisms are described in detail in [25, 28, 29]. As shown in these works, plane gold single crystals without impurities of polycrystalline nanoparticles grow in aqueous solution of HAuCl_4 and PS (final concentration in the mixture is $C_{\text{Au}} = 200 \text{ mg/dm}^3$, and biopolymers – $C_{\text{PS}} = 25 \text{ mg/dm}^3$) at the temperature of $40 \pm 1 \text{ }^\circ\text{C}$ and illumination of 1000 lux. Gold nanoprisms in non-aqueous medium were obtained by the method we have modified [30]. The matched dispersion medium, ratio between concentrations of HAuCl_4 and polyvinylpyrrolidone (PVP), temperature and time behavior of the synthesis allowed to obtain plane nanoprisms of Au with the linear size which is different by 2-3 orders – from tens of nanometers to tens of microns. In this case, the crystal thickness was equal to 40-60 nm.

It is established by the method of electron diffraction and X-ray structural analysis that synthesized nanoprisms have monocrystalline structure, and the X-ray phase analysis has shown that they consist of the gold atoms only (this data is not present in this work).

Rhodamine R6G dye [31-34] which is well studied by the method of Raman spectroscopy, and polymethylmethacrylate (PMMA) [35, 36] were used as the model substances for the demonstration of amplification of the Raman spectrum. In all experiments, solution of rhodamine R6G ($4 \times 10^{-6} \text{ M}$) in anisole ($\text{C}_7\text{H}_8\text{O}$) containing 3% of PMMA was deposited on the surface of gold crystals or glass (control).

Transmission spectra of suspension of gold crystals with respect to the cell with pure dispersion medium were obtained on spectrophotometer produced on the basis of prism quartz monochromator DMR-4. Halogen incandescent lamp KGM-100 acted as the light source. Silicon photodiode FD288 was used as a photodetector. Measurements were carried out in quartz cell of the thickness of 10 mm.

Raman scattering spectra were obtained on the micro Raman spectrometer (Renishaw, RM 1000, objective $\times 50$). Excitation of the Raman scattering spectra was realized by He-Ne laser (excitation wavelength is $\lambda_{\text{exc}} = 632,8 \text{ nm}$). Laser beam was focused on the sample to the spot of the diameter up to $2 \mu\text{m}$. Power of the exciting laser radiation (from 0,2 to 1 mW) for all samples was matched experimentally in order to make luminescent glowing of the sample to be minimum. Accumulation time of the Raman spectrum is 30 sec.

3. RESULTS AND DISCUSSION

3.1 Investigation of the Raman scattering spectra on gold crystals synthesized in aqueous medium

As the earlier performed investigations have shown [25, 29], gold crystals synthesized in aqueous medium are polydisperse and coated by adsorption layer of PS. These biopolymers are both the regenerator of AuCl_4^- ions and stabilizer of the metal phase which is formed again. Thickness of the adsorption layer according to the estimations of [25] can achieve 10-30 nm. As known from publications [10, 31], amplification of oscillations in analyte macromolecule due to the resonant interaction with surface plasmons of the substrate is possible in the case if molecule is located on the distance not more than 10-15 nm far from the metal surface.

Therefore, gold crystals which are used in the given work as the substrate for the SERS-spectroscopy were preliminary washed off from the adsorption layer of PS. To this end, suspension of Au crystals was centrifuged (6000 g, 8000 rpm, centrifuge OPn-8) during 60 min, supernatant which contains free, non-connected with the surface, PS was selected, and sediment of crystals was coated with hot ($\sim 80 \text{ }^\circ\text{C}$) distilled water and resuspended. The obtained suspension was centrifuged again under the same conditions (operation was repeated 4 times). By the atomic-force microscopy (AFM) method it is established [25] that this procedure allows to clean the surface of gold crystals from adsorbed biopolymers.

The obtained aqueous concentrate of washed gold crystals was deposited in the form of a drop on the surface of the preliminary purified cover glass and dried at the room temperature.

The analyzed substance – rhodamine R6G with PMMA – in the form of the solution was deposited on glass with washed gold crystals, and the sample was dried at the room temperature. In Fig. 2 we represent the Raman scattering spectra obtained from the glass surface (curve 1 is the control) and from the surface of gold crystals – curve 2. Micrographs of the regions where the Raman spectra were taken are shown in Fig. 2b.

As seen from Fig. 2a, the Raman spectrum (curve 2) taken from the surface of gold crystals (Fig. 2b-2) has a

number of intensive peaks which are not exhibited in the spectrum (curve 1) obtained from the glass surface (Fig. 2b-1). It is established that intensity of the peak 994 cm^{-1} taken in the "hot point" on gold crystal is increased 10^4 times in comparison with same in curve 1.

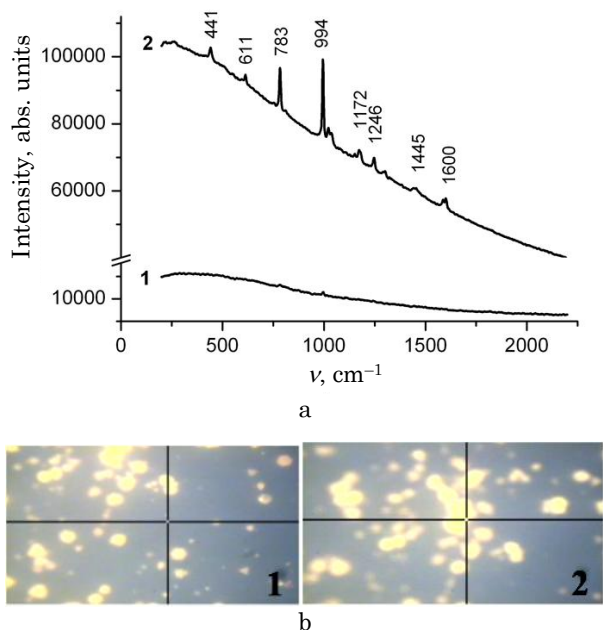


Fig. 2 – a) The Raman spectra of rhodamine R6G with PMMA obtained from the glass surface (curve 1) and from the surface of gold crystals washed from PS (curve 2); b) micrographs of the regions where the spectra 1 and 2 are taken. The laser irradiation power is 1 mW

As a rule, the bands corresponding to the oscillations of those groups of the studied molecule which are maximally approached to the metal surface are amplified in the Raman spectra.

In the first column of Table 1 we present the characteristic frequencies of the Raman spectra main peaks of R6G ($4 \times 10^{-6}\text{ M}$) with 3% of PMMA which are experimentally fixed in the spectra taken from the surface of gold crystals. In order to discuss in detail we give the data of oscillation modes of rhodamine R6G molecule and PMMA which are active in the Raman spectroscopy [31, 35, 36]. Characteristic frequencies of the Raman spectrum of rhodamine R6G molecules amplified by the surface of silver nanoparticles [31-33] are also given for the comparison.

As seen from Table 1, the experimentally determined frequencies of the spectrum main peaks of R6G with PMMA deposited on gold crystals coincide well with the data obtained by the authors of [31-33]. Peak 994 cm^{-1} with maximum intensity, probably, belongs to PMMA. Other vibrational modes do not appear at the given wavelength of the exciting light. According to the data of [31, 33], peak 614 cm^{-1} is connected with C-C-C vibrations in the plane of the R6G molecule ring; peak 774 cm^{-1} – with out-of-plane bend of C-H bond; peak 1183 cm^{-1} – with valent vibrations of C-C bond. Bands $1310, 1363, 1509\text{ cm}^{-1}$ correspond to C-C valent vibrations of aromatic ring of rhodamine molecules.

However, not the whole surface of gold crystal exhibits similar properties to amplification of the Raman signal. This is well demonstrated by a number of spectra taken from different regions of the crystal surface, as well as depending on the arrangement of one crystal with respect to another (see Fig. 3).

The well-focused bands 783 cm^{-1} and 994 cm^{-1} were taken as the reference lines to analyze amplification properties of the surface of gold crystals. The maximum amplification of intensity of these peaks is observed in the case when laser beam is focused on the tip of one gold crystal lying on the surface of another – curve 2 in Fig. 2 and curve 3 in Fig. 3. Comparing in Fig. 3 the

Table 1 – Comparison of the characteristic frequencies in the range of $400\text{-}1600\text{ cm}^{-1}$ of the Raman spectrum of rhodamine R6G molecules ($4 \times 10^{-6}\text{ M}$) in the presence of 3% of PMMA amplified by the surface of gold crystals. For comparison, we present the data for pure R6G, PMMA, and R6G/Ag system

R6G + + PMMA/Au	R6G Data of [31]	R6G/Ag Data of [31]	R6G/Ag Data of [32]	R6G/Ag Data of [33]	R6G/Ag Data of [34]	PMMA Data of [36]	PMMA Data of [35]
441	459	457	–	–	–	–	487
611	614	614	609	613	614	602	604
783	776	774	785	774	774	–	796
994	937	931	934	–	929	999	991
1021, 1036	–	–	–	–	–	–	–
–	1096	1088	–	–	–	1081	–
1151	1131	1129	1137	–	1128	–	1125
1172, 1181	1187	1183	–	1187	1183	–	1161
1246	1271	1268	–	–	–	1264	1234
1291, 1301	1312	1310	1303	1315	1310	–	–
–	1365	1363	1357	1365	1362	–	–
1430	–	1433	1433	–	–	–	1400
1445	1446	1445	–	–	–	1460	1456
1452	–	1472	–	–	–	–	1490
–	1509	1509	1508	1514	1508	–	–
1586	1575	1575	1572	–	1572	–	–
1600	1600	1597	–	–	–	–	–

peak intensity at 994 cm^{-1} in the spectra obtained from the surface of triangular (curve 1) and hexagon gold nanoprism (curve 2), as well as the spectrum obtained from the tip of triangular nanoprism lying on another crystal (curve 3), it is seen that intensity of this band for curves 1 and 2 differs insignificantly ($\Delta I = 3204$ and 3821 abs. units), while intensity of this band in curve 3 is 1,7 times higher than in curve 1 ($\Delta I = 5528$ abs. units). Such difference can be explained by different correlation of contributions of chemical and electromagnetic amplification mechanisms of the Raman signal in each separate case. Increase in the intensity of the band 994 cm^{-1} (Fig. 3, curves 1 and 2) is mainly connected with the adsorption-molecular (chemical) amplification mechanism of the Raman spectrum since there is not local amplification of the field in the case when spectrum is obtained in the point remote from the crystal tips. For spectrum 2 in Fig. 2 and spectrum 3 in Fig. 3, intensity growth of separate bands of the Raman spectrum can be explained by both the interaction of analyte molecules with the surface of gold nanoprism (chemical mechanism) and the electromagnetic mechanism – amplification of oscillations in molecule due to larger intensity of local electromagnetic field near the tips of gold crystal. Theoretical calculations of the electric field of surface plasmon show that on the regions with the maximum surface curvature (in the given case, tip of triangular nanoprism), maximum of the field strength is achieved [17] that leads to amplification of the band intensity of the Raman spectrum.

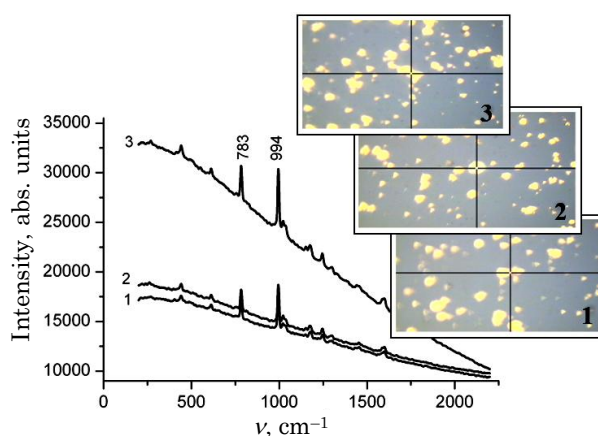


Fig. 3 – The Raman spectra of rhodamine R6G with PMMA from different regions (they are pointed on micrographs, see photos on the insets) of the surface of gold crystals washed from PS. Laser irradiation power is 0,5 mW

One more factor, probably, is exhibited in the case when triangular nanoprism lies on the surface of another crystal. Amplification of electromagnetic field on the upper gold crystal occurs due to the resonant interaction with electromagnetic field because of collective excitation of plasmon modes on the lower crystal that leads to the increase in the amplitude of intramolecular vibrations in analyte molecules, and, as a result, to the change in the band intensity in the Raman spectra.

More uniform distribution of gold crystals on glass surface was obtained when crystals were deposited by

the method proposed in the work [37]. According to this technique, 10 ml of hexane were added to 10 ml of aqueous suspension of Au crystals washed from PS, mixture was mixed, and then acetonitrile was added by drops. In a few minutes, a layer of gold crystals was formed on the water-hexane interface. Film of crystals was raised on the quartz cover glass which was dried at the room temperature, and then the studied substance was deposited on it.

Intensive lines 783 cm^{-1} and 994 cm^{-1} (see Fig. 4) were detected on the Raman spectra of rhodamine R6G with PMMA adsorbed on such substrates. More uniform distribution of gold crystals on glass surface gives the possibility to obtain spectra with almost the same band amplification (see curves 1 and 2, Fig. 4) from different sample regions.

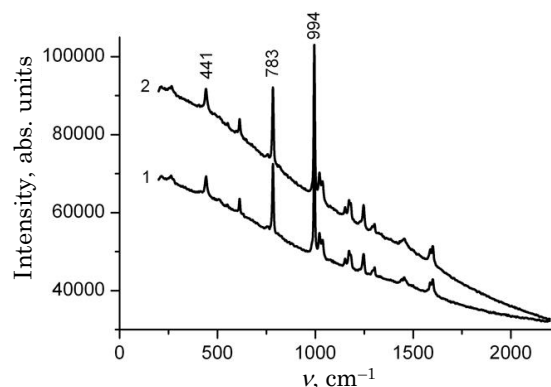


Fig. 4 – The Raman scattering spectra of rhodamine R6G with PMMA adsorbed on the surface of Au crystals washed from PS obtained from different regions of the glass substrate with crystals. Laser irradiation power is 0,5 mW. Film of Au crystals is deposited on cover glass made of the crystals-water-hexane-acetonitrile mixture

Amplification of these band implies that crystal surface is well cleaned from adsorption layer of PS (hexane and acetonitrile are vaporized at drying), and molecules of the studied substance are adsorbed on the cleaned gold surface.

Increase in the intensity of the bands 783 cm^{-1} and 994 cm^{-1} can be induced by both the local amplification of electromagnetic field in “hot points” of gold nanocrystals at focusing of the incident light beam on their tips and due to the adsorption-molecular interaction of R6G molecules and PMMA with gold.

3.2 Investigation of the Raman spectra on gold crystals synthesized in non-aqueous medium

As the performed investigations have shown, synthesizing gold crystals in non-aqueous medium, one can govern both the linear size of nanoprisms and obtain higher percentage yield. Polyvinylpyrrolidone added to disperse medium determines the morphology of formed Au crystals and prevents their aggregation. At initial concentration of gold $C_{Au} = 100\text{ mg/dm}^3$ in the ethylene glycol and ethyl alcohol mixture, gold nanoprisms of the mean linear size of $12\text{--}18\text{ }\mu\text{m}$ – large crystals (Au-100) (see Fig. 1d) are formed during 24 hours at $80\text{ }^\circ\text{C}$.

At concentration of 0,25 mM of HAuCl_4 in the medium ($C_{\text{Au}} = 50 \text{ mg/dm}^3$), fine gold crystals (Au-50) (see Fig. 1c) are obtained during 5 hours at the same synthesis conditions. In this case, nanoprisms have bimodal behavior of the distribution over liner size: a part of crystals has the mean size of $\sim 300 \text{ nm}$, and another – of $\sim 900 \text{ nm}$.

As known [20], the particle size and shape influence the energy excitation spectrum of surface plasmons. Therefore, the optical properties of synthesized gold crystals were investigated. In Fig. 5 we show the transmission spectra in the wavelength range of 360-1060 nm of suspension of crystals Au-50 synthesized again (curve 1) and after 120 days of their storage in a dark place in the mother medium at the room temperature – curve 2. As seen, on the initial stage absorption peak induced by excitation of local plasmons is very wide that can be explained by polydispersity of the obtained crystals. After 120 days larger nanoprisms were sedimented, and fine ones remained in the volume. This is represented in the second spectrum where peak became narrower and shifted to the short-wave region.

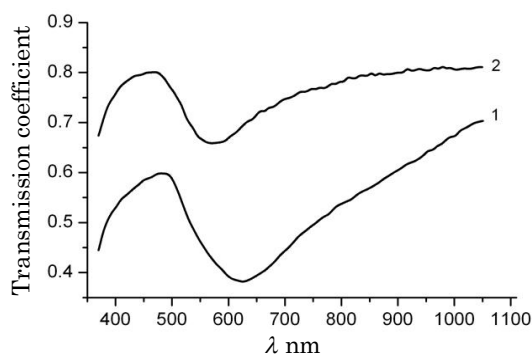


Fig. 5 – The transmission spectra of colloidal suspensions of Au-50 crystals in the mother (non-aqueous) medium: curve 1 – suspension after synthesis; curve 2 – suspension after 120 h

Excitation frequency 632,8 nm of the Raman signal coincides with the absorption maximum of suspension of initial crystals Au-50 (see Fig. 5, curve 1). Probably, strong light absorption by Au crystals in this region promotes amplification of the local electromagnetic field on nanoprisms Au-50 deposited on a glass surface.

Au crystals washed from adsorbed PVP layer were used for surface-enhanced micro Raman spectroscopy. To this end, they were separated from mother disperse medium by centrifugation (6000 g, 60 min); then they were washed for 4 times by distilled water, and concentrate was resuspended in distillate. Film of washed Au crystals was deposited on a cover glass, dried at the room temperature, and then covered by the solution of rhodamine R6G with PMMA in anisole. Raman spectra were excited by focusing a laser beam on different regions of dried substrate with gold crystals and without them (control).

In Fig. 6a we represent the Raman spectra of rhodamine R6G ($4 \times 10^{-6} \text{ M}$) with PMMA obtained from the surface of Au-100 crystals washed from PVP; in Fig. 6b – micrographs of the regions from which these spectra were obtained. The laser irradiation power of the sample was equal to 1 mW, other conditions of the experiment were the same as in the previous cases.

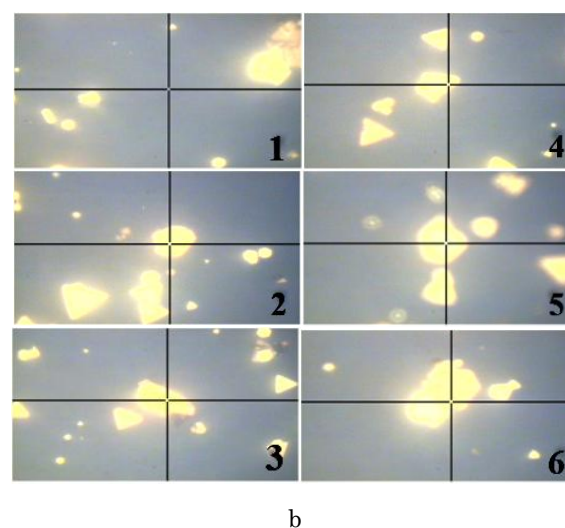
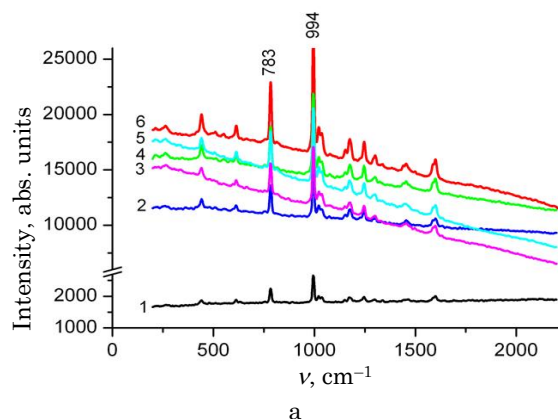


Fig. 6 – a) The Raman spectra of rhodamine R6G with PMMA obtained from the surface of Au-100 crystals washed from PVP; b) micrographs of the regions from which the spectra are taken. Laser irradiation power of the sample is 1 mW

The Raman spectra (Fig. 6a, curve 1) obtained from the region without crystals (see Fig. 6b-1) demonstrates the bands 783 and 994 cm^{-1} of insignificant intensity which are sharply amplified by the surface of Au-100 crystals – spectra 2-6.

Fine crystals of Au-50 for the amplification of the Raman spectra were prepared by the same technique. However, separation factor of 6000 g at centrifugation is not enough to deposit all Au-50 crystals; therefore, a part of finest crystals was lost at washing from PVP. One could not form a uniform coating of washed Au-50 crystals on the glass surface: both the single crystals and their aggregates were observed. In Fig. 7 we show the Raman spectra of rhodamine R6G with PMMA obtained from the glass surface (curve 1) and amplified by the surface of Au-50 crystals (curve 2 and curve 3).

As seen in Fig. 7, the Raman spectrum (see curve 3) excited by the laser beam focused on the aggregate of crystals demonstrates amplification of separate peaks which are not exhibited at all on the spectrum obtained from the glass surface (curve 1) and were not observed earlier on the surface of large crystals Au-100. These bands are also not connected with polyvinylpyrrolidone which, as one can suggest, remained on the surface of Au-50 crystals. Appearance of a new intensive band in the Raman spectrum (Fig. 7, curve 3) can be explained

by the excitation of forbidden Raman lines because of the change in the rules of selection due to the amplification of electric field on the tips of nanoprisms Au-50 through their strong polarization [38, 39] or nanosize gradient of electric field connected with localized surface resonance [40, 41].

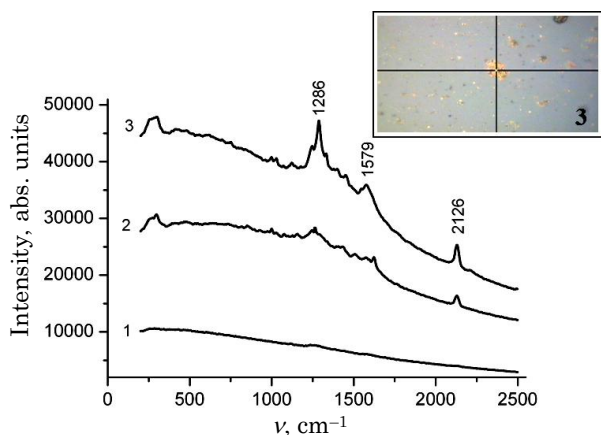


Fig. 7 – The Raman spectra of rhodamine R6G with PMMA obtained from the surface of Au-50 crystals washed from PVP (on the inset – micrograph of the region from which spectrum 3 is taken). Laser irradiation power of the sample is 0,2 mW

We would like to discuss one more feature of this experiment. Seemingly, in the case of fine gold crystals, the most quantity of them should be on the region from which the Raman spectrum is obtained, and intensity of the peaks should be sharply increased. However, the value of intensity of the strongest peak in curve 3 (see Fig. 7) is comparable with the intensity of the band 994 cm^{-1} (curve 6 in Fig. 6). This discrepancy can be explained by the following. When gold nanoprisms are aggregated and chaotically located with respect to each other, then surface plasmons of separate crystals are combined and generate modes which envelope the whole

aggregate and cover a wide frequency range, and as a result – there is no assigned resonant mode and resonant amplification of oscillations in the studied molecule. Therefore, for fine gold crystals it is very important to have their uniform distribution on the substrate (the problem of further investigations), for example, as it was done for silver nanowires by the method of the Langmuir-Blodgett films [34, 42] and register the Raman signal in “hot points”.

4. CONCLUSIONS

It is shown in the present work that synthesized in aqueous and non-aqueous media and washed from adsorption layer of stabilizer gold crystals of the shape of equilateral triangles, truncated triangles, and hexagon nanoprisms can be used as the substrate for the amplification of the Raman spectra. By the method of micro Raman spectroscopy we have demonstrated $\sim 10^4$ -fold amplification of the intensity of separate bands of the Raman spectra of rhodamine R6G dye and PMMA in the case of laser beam focusing on the tip of triangular nanoprism of a separate crystal or on the tip of a nanoprism lying on the surface of another crystal. Such increase in the intensity is caused by the electromagnetic amplification mechanism, namely, by the local increase in the electromagnetic field on the crystal tip where there is a sharply pronounced non-uniformity of the surface. Increase in the peak intensity of the Raman spectrum taken from the surface of gold nanoprism far from its tip occurs, mainly, because of the adsorption-molecular amplification mechanism of the Raman spectrum due to the increase in the cross-section of the Raman scattering of analyte molecule which is adsorbed on the surface of Au crystal cleaned from stabilizer, i.e. chemical amplification mechanism dominates over electromagnetic one.

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