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CONTROLLED AGGREGATION OF PLASMONIC NANOPARTICLES TO ENHANCE THE EFFICIENCY OF SERS SUBSTRATES

A possibility of creating universal and effective SERS substrates via controlled aggregation of gold and silver colloidal nanoparticles (NPs) on substrates with a specially developed surface morphology has been demonstrated. Unlike the previous work on the development and research of SERS substrates, in which the enhancement was mainly realized on separate protruding nanoparticles or nanoislands, the change to the multilevel substrate structuring and the controlled aggregation of the deposited colloidal plasmonic NPs substantially increases the formation probability of hot spots and getting analyte molecules onto them. The efficiency of the proposed approach has been demonstrated for several organic analytes of various types, in particular, the R6G dye, the cysteine amino acid, and antibodies.

Keywords: SERS substrates, Raman spectroscopy, R6G, biomolecules.

1. Introduction

Despite that the possibility of registering a Raman spectrum from a single molecule has already been demonstrated [1], the number of works devoted to the study of vibrational spectra of various substances making use of the surface-enhanced (or giant) Raman scattering (SERS) method and by means of the direct study of the mechanisms of Raman enhancement has been steadily growing every year. It occurs due to several factors. Firstly, this is the necessity of obtaining a Raman signal from an extremely small amount of substance, which is realized by depositing the molecules onto SERS substrates or by plasmonic enhancement of the Raman signal generated by them in solutions. Secondly, this is the necessity of understanding the features in the manifestations of the mechanisms of electromagnetic (EM) and chemical enhancement of the Raman signal. Thirdly, this is the necessity of developing universal and relatively in-

expensive SERS substrates capable of enhancing the Raman signal from various substances.

Nowadays the detection of extremely small amounts of the substance is a very urgent task in many domains of science and human life. As examples we can point to chemistry and pharmacology while synthesizing new substances, criminology, medicine at the early diagnosis of dangerous diseases (especially cancer), biology, ecology, materials science, safety, and so forth [2–9].

The SERS process involves the complex interaction of three objects: photons, targeted molecules, and metal nanostructures forming the basis of SERS substrates. The latter can be classified into two main categories: structured metal surfaces and metal NPs precipitated from colloidal solutions [10–17].

The most important manifestation of the EM enhancement of the SERS signal from the examined substances is a considerable growth of the electric field in which they are located, which occurs due to both the excitation of plasmons in nanostructured metals and the formation of so-called “hot spots” as a result of superposition of electric fields generated by several metal NPs arranged at a nanometer dis-

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tance from one another. The chemical enhancement of the Raman signal takes place due to the change in the polarization of studied molecules and, if a chemical bond is formed between the molecules of the researched substance and metal NPs, the charge transfer effect. The latter gives rise to a modification in the electronic structure of molecules, and this modification can manifest itself both in the shift of electron levels and in the emergence of new ones. As a result of the resonance Raman scattering between “new” electron levels, the selective enhancement of separate vibrational bands takes place. This is in contrast to the EM mechanism at which the bands become approximately identically enhanced in a wide spectral interval [18].

The mechanism of electromagnetic enhancement is much more efficient than the chemical one. It is also more universal with respect to the type of analyte because it does not require the matching of the electronic levels in the metal and the analyte molecule. Especially effective is the realization of the EM enhancement based on the formation of “hot spots”, which is the subject of this work. More specifically, this is the formation of “hot spots” via the controlled aggregation of gold or silver colloidal NPs on substrates with a specially developed morphology by introducing ions of a definite sign into the solution. The detection efficiency can be improved further, if, instead of flat surfaces of glass or silicon substrates, metalized surfaces structured at the micron or submicron scale will be applied, which will prevent the formation of so-called “coffee rings”, thus favoring a more uniform distribution of metal NPs and analyte molecules over their surfaces. Furthermore, such a morphology can also promote the excitation of delocalized plasmons (owing to the reduction of the angle between the excitation laser beam and the metal surface) and, as a result, an additional enhancement of the Raman signal.

2. Experimental Part

The preparation of micron-structured surfaces was performed on the surface of purified glass or silicon plate by thermal sputtering of copper or aluminum layers to a thickness of several micrometers through a special mask. The next step in the preparation of structured substrates consisted in the sputtering of a silicon dioxide layer. The latter played the role of

dielectric isolation of the metal basis from the next layer of precious metal, in which plasmon excitations should be generated. A thermally sputtered thin (about 10 nm) gold layer was optionally subjected to thermal annealing at 450 °C for 10 min to form plasmonic NPs. For specimens not subjected to such annealing, a continuous gold layer was used to excite delocalized plasmons and make them interact with local plasmon excitations in colloidal metal NPs deposited at the next stage.

The synthesis of silver and gold colloidal NPs was carried out on the basis of the known reduction method of metal ions in the presence of sodium citrate [19–21]. The controlled aggregation of NPs was ensured by adding salts that are capable of dissociation in water at room temperature, in particular, NaCl, CsCl, AgNO₃, and Ni(NO₃)₂.

The morphology of SERS substrates was studied using a Leica CME BINOCULAR 100x Oil optical microscope and a Tescan Mira 3 LMU scanning electron microscope (SEM).

Raman studies were performed at room temperature on a spectrometer composed of a monochromator equipped with a CCD camera (Andor®). Solid-state laser radiation with wavelengths of 457, 532, and 671 nm was used to excite Raman scattering. R6G solutions with various concentrations, the cysteine amino acid, and antibodies to the Escherichia coli (*E. coli*) pathogen were used as analytes. They were deposited in the same amount (5 μl) – making use of a dispenser – on the surface of the SERS and reference (glass and silicon) substrates and then dried in the air atmosphere. SERS and Raman spectra were excited by laser radiation, the power of which was minimal but sufficient for the reliable registration of the spectra. This requirement was associated with the fact that degradation of the studied substances can occur under intensive laser radiation due to both their heating and photochemical reactions in them. To verify the homogeneity of SERS substrates, the spectra were registered at several points for each type of substrates.

3. Results and Their Discussion

In this work, the formation of SERS substrates consisted in the controlled aggregation of gold and silver colloidal NPs on substrates with the specially developed surface morphology. The results of the study of

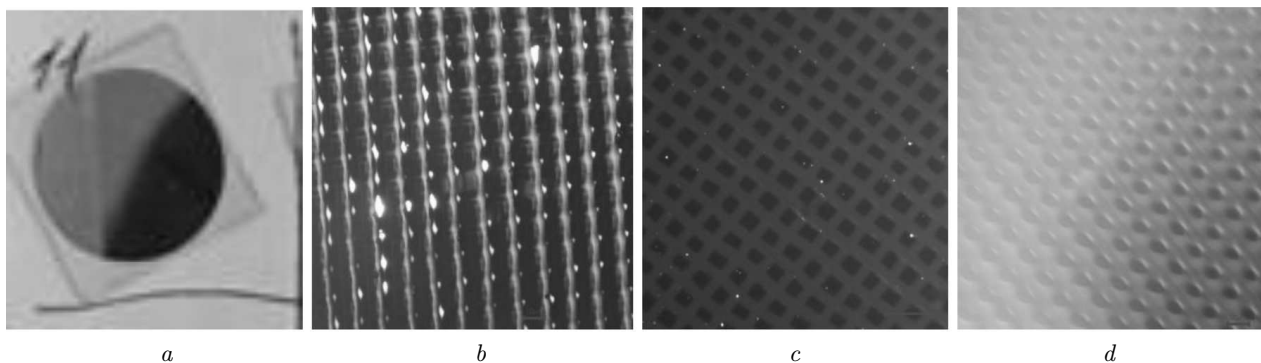


Fig. 1. General view of the obtained copper substrates on glass; the digital image was registered via an optical microscope (a). More detailed images obtained for specimens with various nominal thicknesses of copper layer (b–d)

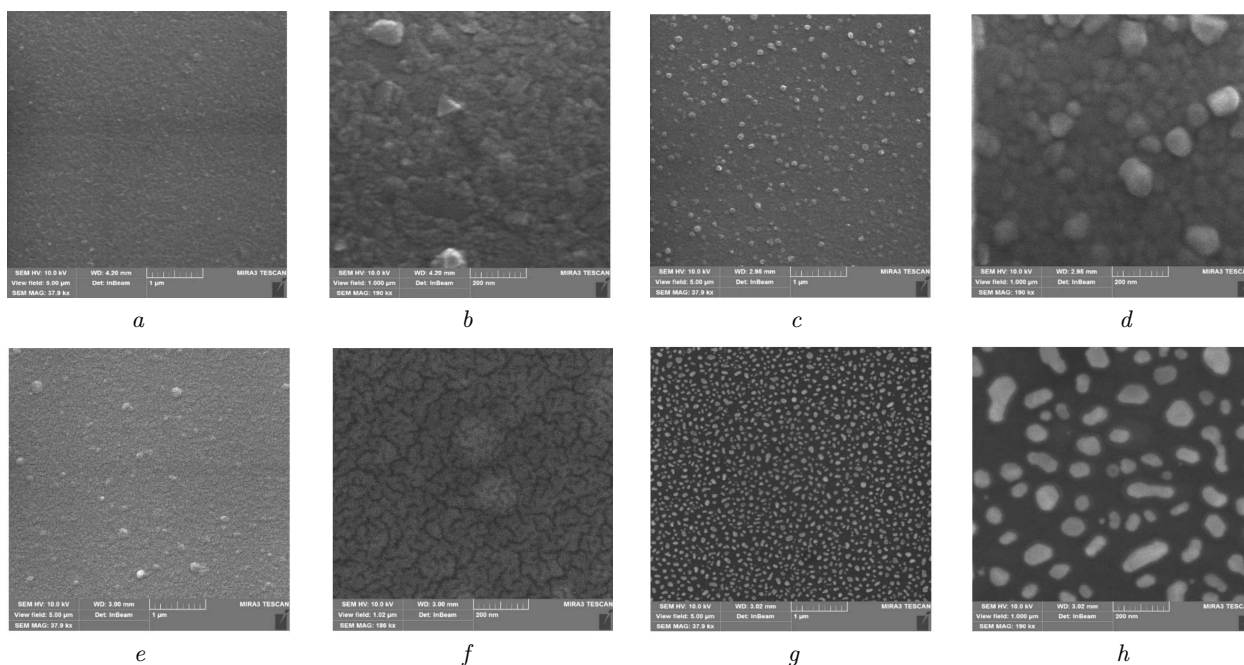


Fig. 2. SEM images of aluminum-based SERS substrates at various production stages and two magnifications: initial aluminum layer (a, b), deposited SiO_x layer and 10-nm gold layer (c, d), Al/ SiO_x /Au structure after thermal annealing at 450°C for 10 min (e, f)

substrates with the specially microstructured surface making use of optical microscopy are illustrated in Fig. 1. From these images, one can see that the variation of the nominal thickness of the deposited copper layer from a few micrometers (Fig. 1, b) to several tens of micrometers (Fig. 1, d) substantially affects the morphology of the substrate surface. The application of such microstructured substrates instead of glass or silicon substrates with a flat surface aims at obtaining a more uniform distribution of analyte over their sur-

faces and at a formation of additional “hot spots” that can be deposited on such substrates together with the analyte. Furthermore, such a morphology can favor the excitation of delocalized plasmons and, therefore, a further enhancement of the Raman signal.

Figure 2 demonstrates SEM images obtained at various preparation stages of aluminum-based substrates. The images are also shown at various magnifications. In particular, in Figs. 2, a and b, the surface of the initial aluminum layer is shown, whereas

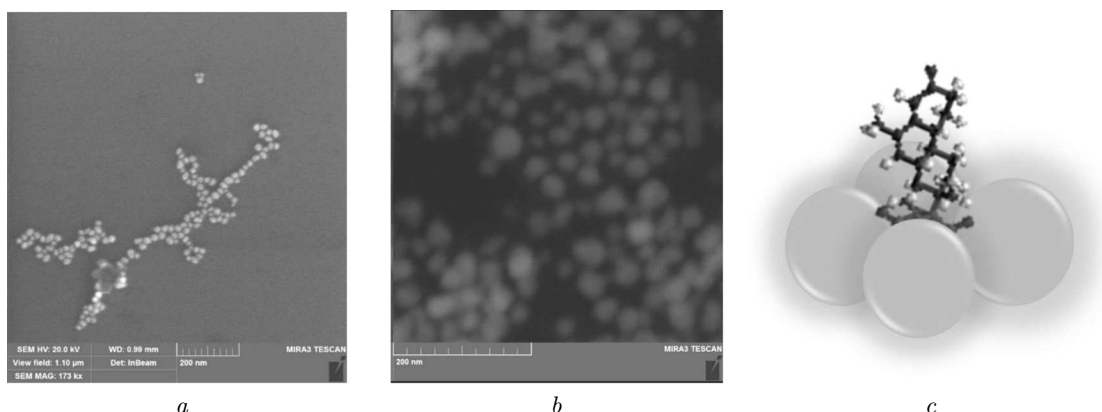


Fig. 3. Substrate surface nanostructured with gold (a) and silver (b) colloidal NPs. Schematic representation of the “hot spot” formation on the SERS substrate surface structured with nanospheres for which plasmon resonance is inherent (c)

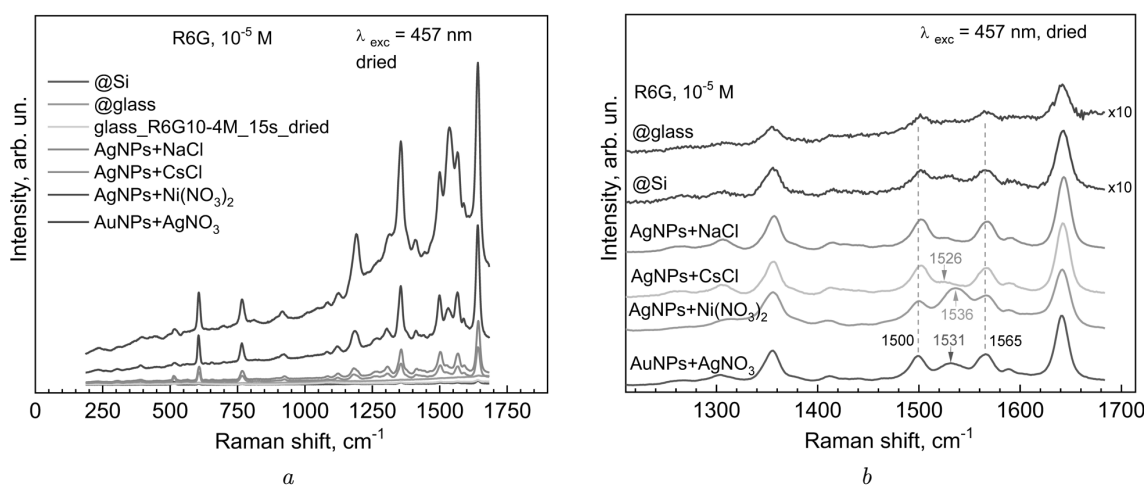


Fig. 4. SERS spectra of analyte (R6G) molecules precipitated from the aqueous solution with a concentration of 10^{-5} M: non-normalized spectra (a), spectra normalized by the band intensity at 1350 cm^{-1} (b)

Figs. 2, c and d illustrate the surface morphology after the deposition of a thin (10–20 nm) SiO_x layer. After the sputtering of a gold layer to a thickness of approximately 10 nm, a typical nanometer-scale labyrinthine structure is formed (Figs. 2, e and f). Annealing of such a multilayer structure $\text{Al}/\text{SiO}_x/\text{Au}$ at a temperature of $450\text{ }^\circ\text{C}$ for 10 min leads to the formation of island-like morphology already possessing the plasmon resonance properties in the visible spectral interval [14, 15].

In this work, in order to improve the efficiency of SERS substrates, the precipitation of gold or silver colloidal NPs (Figs. 3, a and b) was performed. The aggregation agents were preliminary added to the col-

loidal solution in the form of salt solutions that easily dissociate in water. Positively and negatively charged ions formed at dissociation not only induce the controlled aggregation of metal NPs to form “hot spots” (Fig. 3, c) but they can also improve the adsorption of a certain analyte onto the aggregate surface [22, 23]. If AgNO_3 is added, an extra enhancement of the signal can be expected owing to the photoinduced formation of new silver nanoparticles in the course of Raman measurements.

As a test object for the developed SERS substrates, we used the rhodamine 6G dye (R6G), which is not only a standard analyte for demonstrating the efficiency of SERS substrates [24] but also a Raman

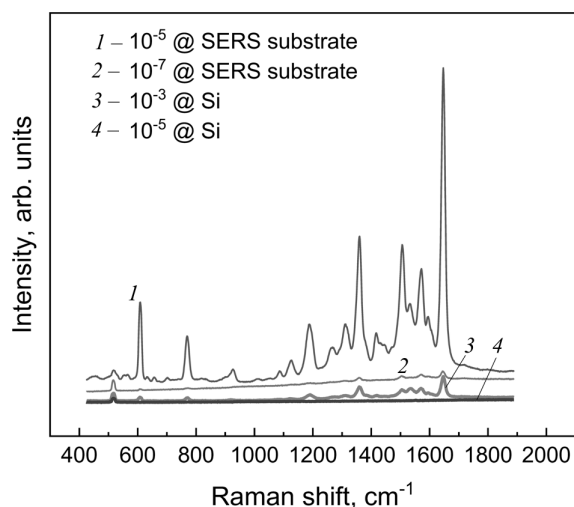


Fig. 5. SERS spectra obtained in this work for R6G molecules with various concentrations ($\lambda_{\text{exc}} = 457 \text{ nm}$). Analogous spectra obtained in the case with silicon substrates are also given for comparison

marker for the SERS detection of biomolecules that do not reveal sufficient intrinsic Raman activity even under effective plasmon enhancement [25]. The maximum enhancement was observed for SERS substrates obtained by aggregating metal NPs with nitrates (Fig. 4, *a*). The comparable enhancement level in the cases of nickel and silver nitrates testifies that the enhancement is achieved just owing to the action of ions as aggregating agents rather than additional plasmonic NPs formed as a result of photoreduction of metal ions. A slightly stronger enhancement in the case of nickel nitrate may be associated with the number of nitrate ions that is twice as large as the same parameter in the case of silver nitrate provided that the concentrations of their molecules are identical.

Our results allow us to conclude that the cation type can affect not only the intensity of Raman signal but also its spectral characteristics, i.e., the relative band intensity. In particular, the band with a maximum at $1531\text{--}1536 \text{ cm}^{-1}$ has an appreciably higher intensity in the cases with nitrates than in the cases with NaCl and CsCl (Fig. 4, *b*). Such spectral differences may testify to different adsorption geometries of analyte molecules in the presence of ions with different charge signs and values [26], as well as to the contribution of the chemical mechanism of SERS enhancement, which is directly related to the distribution of electric charges in the NP-analyte system

[18]. This issue requires a further in-depth study with the help of a wider scope of spectroscopic methods.

It is worth noting the following feature in the SERS spectra: the non-proportional dependence of the total intensity of the bands on the concentration of studied molecules in the solution (Fig. 5). In particular, if the concentration of rhodamine was changed by two orders of magnitude (from 10^{-7} M to 10^{-5} M), one might expect that the intensity of the bands in the SERS spectra would also change by a factor of 100. However, the intensity measurements of the most intensive band (at about 1646 cm^{-1}) showed that the intensity grew by a factor of only 40. It seems that the efficiency of SERS substrates is different for the precipitation of molecules from solutions with different concentrations. This fact can be explained as follows. At low solution concentrations, the substrate is not completely covered with molecules, and only a certain concentration of R6G molecules in the solution provides the complete coverage (as a monolayer) of the SERS substrate at their precipitation on its surface. A further growth of concentration leads to the formation of additional layers of molecules on the monolayer top. It is clear that the largest contribution to the SERS enhancement is given by the first layer of molecules, and the contribution of other layers decreases as r^{-10} , where r is the distance from gold NPs to the analyte [18]. Since the intensity of the bands in the SERS spectrum is a superposition of scattering from every layer, it is clear that the total intensity of the bands given by 10 layers will not be even twice as large as the intensity given by the monolayer. The calculations showed that R6G molecules with an effective area of about 1.51 nm^2 completely cover, as a monolayer, the substrate surface at a solution concentration of 10^{-6} M . Whence it is clear why the band intensity increased only by a factor of 40 when the solution concentration increased from 10^{-7} M to 10^{-5} M .

In our previous work [8], this problem was studied in a wider concentration interval of a standard analyte on the basis of CV molecules precipitated onto plasmon substrates. The latter were layers of gold “nano-stars”. A considerably larger “lag” in the growth of the intensity of SERS bands with respect to the growth of the concentration of molecules precipitated onto SERS substrates consisting of “nano-stars” was revealed as compared with the results of this work. In particular, the band intensity increased by a factor

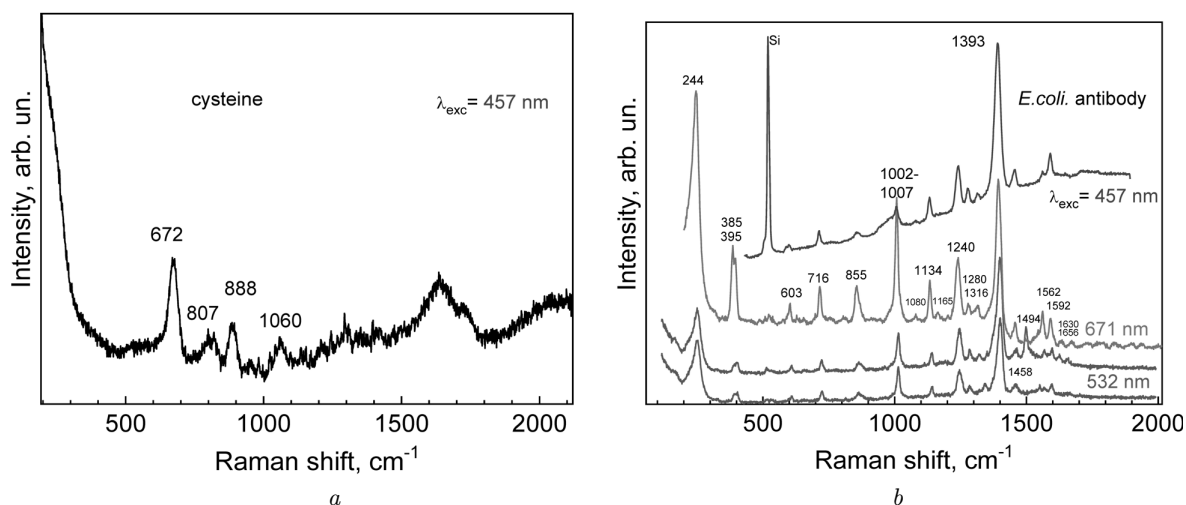


Fig. 6. SERS spectra of biomolecules obtained using SERS substrates developed in this work: cysteine SERS spectrum ($\lambda_{\text{exc}} = 457$ nm) (a) and SERS spectra of *E. coli* antibodies at various λ_{exc} (b)

of 6 if the concentration of CV molecules increased from 10^{-8} M to 10^{-7} M, and only by a factor of 1.5 if the concentration of CV molecules increased from 10^{-5} M to 10^{-4} M. Naturally, the following question arises: Why the intensity of the bands in the SERS spectrum does not increase linearly with the concentration variation even at low concentrations (for example, in the interval from 10^{-8} M to 10^{-7} M), when a monolayer has not been formed yet?

If the solution concentration increases by an order of magnitude, the number of molecules adsorbed on the gold NPs also increases by an order of magnitude. At the same time, the growth of the band intensity in the SERS spectra by a factor of only 6 may testify that not all CV molecules were enhanced identically. In other words, there is a nonlinear relation between the number of molecules and the intensity of SERS signal, which may be associated with the formation of “hot spots”. Thus, the more linear growth of the intensity of Raman bands of the analyte, which was obtained in this work, brings us to a conclusion that now we had more “hot spots” as compared with previous works and/or more uniform and efficient distributions of those points and analyte over the surface of SERS substrate. In the previous works, we repeatedly marked that, for certain types of SERS substrates, it is “hot spots” that provide the main contribution to the signal enhancement [27].

The scanning of SERS signals over the substrate surface areas located at the center of the spots showed

that the spectral intensities are different by no more than 5–10% between the SERS substrates of both types, which testifies to their surface homogeneity. Neglecting the effects of surface wettability in the solutions, we calculated the surface concentration of the examined molecules on the substrates. It is known that the SERS signal enhancement coefficient is determined according to the formula [18]

$$k = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{RS}}/N_{\text{RS}}},$$

where I_{SERS} and I_{RS} are the intensities of SERS and normal Raman signals, respectively, and N_{SERS} and N_{RS} are the numbers of molecules contributing to the SERS and Raman scattering, respectively.

The approach to the formation of SERS substrates, which was proposed in this paper, makes it possible to obtain signal enhancement from various types of analytes, in particular, biomolecules, as is shown in Fig. 6 by the example of cysteine amino acid molecules (panel a) and *E. coli* antibodies (panel b).

4. Conclusions

To summarize, a possibility of creating universal, inexpensive, and effective SERS substrates via controlled aggregation of gold or silver nanoparticles (NPs) on substrates with a specially developed surface morphology has been demonstrated. Unlike most earlier works on the development and research of

SERS substrates, where the enhancement was mainly realized on separate NPs or nano-islands, the multi-level structuring of the substrate and the controlled aggregation of colloidal plasmonic NPs precipitated onto it substantially increase the probability for “hot-spots” to emerge and the probability for analyte molecules to reach them. From a more linear growth of the intensity of the analyte Raman bands, which was obtained in this work, a conclusion can be drawn that now we had more “hot spots” in comparison with our previous works and/or more uniform and efficient distributions of those spots and analyte molecules over the substrate surface. The efficiency of the proposed approach has been demonstrated by the examples of the standard analyte (R6G) and the organic analytes of various types, in particular, the cysteine amino acid and *E. coli* antibodies.

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КОНТРОЛЬОВАНА АГРЕГАЦІЯ ПЛАЗМОННИХ НАНОЧАСТИНОК ДЛЯ ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ SERS-ПІДКЛАДОК

У роботі продемонстровано можливість створення універсальних та ефективних SERS-підкладок шляхом контрольованої агрегації колоїдних наночастинок (НЧ) золота та срібла на підкладках зі спеціально розробленою морфологією поверхні. На відміну від більшості попередніх робіт по розробці та дослідженню SERS-підкладок, в яких підсилення реалізується переважно на оремих НЧ чи наноострівцях, перехід до багаторівневого структурування підкладки та керованої агрегації осаджених на неї колоїдних плазмонних НЧ суттєво збільшує ймовірність утворення "гарячих точок", а також потрапляння в них молекул аналіту. Ефективність запропонованого підходу продемонстрована на кількох органічних аналітах різного типу, зокрема, барвнику R6G, амінокислоті цистеїн та антибіотиках *E. coli*.

Ключові слова: SERS-підкладки, раманівська спектроскопія, R6G, біомолекули.