

Influence of atomic- and micro-roughness variations on the surface enhanced Raman scattering signal

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Atomic scale roughness of an electrode on which the Surface Enhanced Raman Scattering (SERS) occurs may be altered by variation of the electrode potential, its temperature as well as by illumination. Whereas the size of micro-roughness of the electrode may be changed by variation of parameters of the oxidation-reduction procedure. Variations of both mentioned types of roughness cause changes of SERS signal. These changes prove for the electromagnetic and chemical origin of the enhancement in the SERS phenomenon.

1. Introduction

Surface Enhanced Raman Scattering (SERS) is observed on surfaces of some solid metals as well as on their colloidal particles. The theoretical and experimental search of mechanisms responsible for the observed huge enhancement of Raman scattered light in SERS is still intensively continued. On the basis of vast experimental results several possible mechanisms of enhancement have been proposed, however, none of them can explain that effect individually and completely [1]–[3]. At present, most investigators agree that SERS is a result of two mutual complementary mechanisms: the classical electromagnetic enhancement mechanism (CEME) and the chemical one [4]–[7]. The CEME model assumes that the enhancement of Raman scattering is a result of the enhancement of electric field of both incident and scattered light caused by the rough surface. The initially smooth surface, after roughening procedure, acquires bumps which can be approximated to spheres, hemispheres and prolate spheroids. From the solution of electrodynamic equation it follows that the electric field of the incident and scattered light is enhanced inside the micro-objects [3], [7], [8]. The magnitude of this enhancement depends on the size and shape of surface micro-objects and on the imaginary part of the surface dielectric function. The giant gain is theoretically expected when:

- i) micro-structures are of small sizes, *i.e.* the semi axes of micro-objects are much lower than the wavelength of exciting light,
- ii) micro-objects are prolonged, *i.e.* a/b ratio is large, where a , b are the semi-axes perpendicular and parallel to the metal plane, respectively,
- iii) the imaginary part of the dielectric function of the metal is small for the frequency of exciting light (the largest enhancement is obtained when the frequency of the exciting light is equal to the frequency of the localized surface plasmon).

The SERS enhancement observed on the surfaces which fulfil conditions i)–iii) is, however, larger than that predicted by CEME model. One may then expect that there exists another mechanism responsible for the additional enhancement. The chemical mechanism called alternatively charge transfer (CT) or “adatom” or “active site” mechanism is additionally responsible for the enhancement [3]–[7], [9]–[11]. The CT model requires the existence of adatoms (*i.e.* single atoms or clusters) on the surface. The surface on which adatoms exist is called the rough surface in atomic scale. The CT model assumes that the complexes of adatom-adsorbed molecule with charge transfer interaction are formed at the surface. These complexes may produce the resonance Raman scattering. The latter occurs if the energy of exciting light is equal or close to the difference between the ground and excited state energies (ΔE_{CT}) for the charge transfer complex. It is now generally accepted that both the CEME and CT mechanisms determine the experimentally observed SERS signal.

In this work, we demonstrate the influence of the electrode potential, temperature, illumination, time and micro-roughness on the magnitude of SERS signal. We explain the observed dependences on the basis of CEME and CT models of SERS enhancement.

2. Experimental

SERS investigations were performed in three-electrode electrochemical cell. The experimental set-up used for observation of SERS phenomenon was similar to that described in previous work [12]. A polished mirror polycrystalline silver disc of 6 mm diameter was used as a working electrode and placed in the centre of a cylindrical glass cell. The circular Pt-wire was used as a counter electrode. All potentials were referred to the saturated calomel electrode (SCE) located in the proximity of the working electrode. The 0.1 M aqueous solution of KCl containing 0.05M pyridine was used as electrolyte.

For heating of the working electrode, the electrochemical cell was placed inside a temperature controlled oven. The construction of the oven enabled the light to freely penetrate the electrochemical cell. Close to the working electrode a thermosensitive element was immersed for the measurement of electrode temperature. The oven together with the thermosensitive element permitted us to stabilize the temperature of the electrolyte and electrode in the range from 278 to 363 K.

The 514.5 nm line of ILA-1 Ar⁺ ion laser was used for the SERS excitation. The power of the laser beam introduced to the electrochemical cell was equal to 200 mW. The laser beam was directed on the surface of the working electrode at the angle of incidence of 60°. The light scattered on the electrode was focused on the entrance slit of a double grating monochromator. The effective band pass of the monochromator slits was 4 cm⁻¹. The cooled photomultiplier (M12FQ51) and the photon counting system used for SERS spectra detection.

For the qualitative estimation of roughness of the electrode, the angle distribution of the intensity of elastically scattered light was measured. The measure-

were carried out as follows. The collimated laser beam (4 mm diameter) was directed perpendicularly on the surface of the dried electrode kept outside the electrochemical cell. The intensity of elastically scattered light was measured by the photomultiplier which was placed at the distance of 0.5 m from the electrode and it could be rotated in the plane perpendicular to the plane of electrode. The rotation of the photomultiplier permitted measurements of the intensity of scattered light as a function of scattering angle. The signal from photomultiplier was recorded and analysed by PC computer.

3. Results and discussion

3.1. SERS intensity dependence on electrode potential

For SERS activation of the silver surface, it is necessary to perform at least one oxidation-reduction cycle (ORC). During the ORC the current and the SERS intensity were measured as functions of the potential V_{SCE} . The results of these measurements are presented in Fig. 1. Voltammograms and voltramanograms are plotted by dashed and solid lines, respectively. The curves in Fig. 1a are obtained for the potential sweep in the range of -1.20 – $+0.13$ V, while in Fig. 1b in

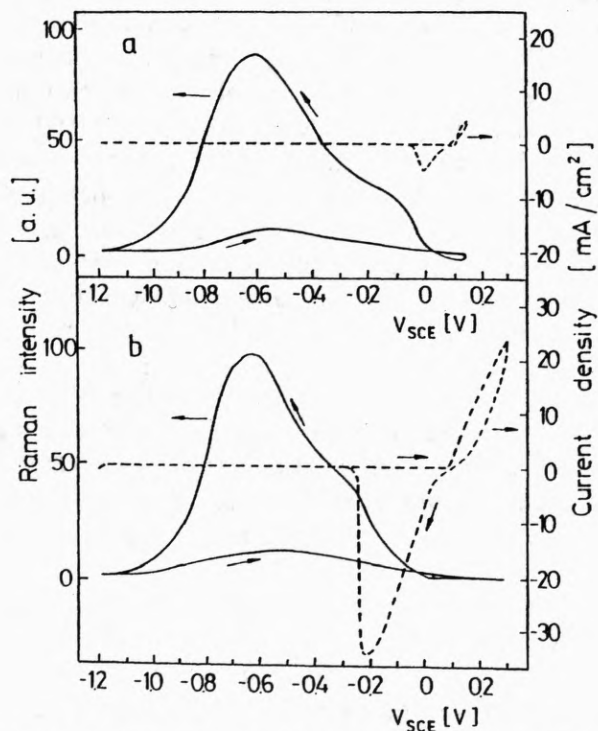


Fig. 1. Cyclic voltammograms (dashed line) of Ag electrode in 0.05 M pyridine and 0.1 M KCl aqueous solution and SERS voltramanograms (solid lines) of 1008 cm^{-1} band of pyridine adsorbed on Ag electrode for the potential sweep in the range from -1.20 to $+0.13$ V (a), and from -1.20 to $+0.30$ V (b). The potential sweep rate was equal to 5 mV/s and the power of 514.5 nm laser line was 200 mW

-1.20- +0.30 V. The strongest band (1008 cm^{-1}) SERS spectrum of pyridine was used for recording of these voltammograms. From presented voltammograms it follows that the SERS signal depends on the electrode potential and direction of the potential sweep. The detectable SERS signal appears as soon as the reduction of early oxidized electrode begins and increases during the reduction procedure. After the termination of electrode reduction, during the decrease of the potential V_{SCE} , the SERS signal reaches the maximum for $V_{\text{SCE}} = -0.60\text{ V}$. The continuation of potential fall causes the decrease of SERS signal. At the potential $V_{\text{SCE}} = -1.20\text{ V}$, the SERS signal becomes undetectable. The renewed increase of the V_{SCE} causes the increase of SERS signal, but now it is smaller than in the case of decreasing potential. Now, the maximum is attained again at $V_{\text{SCE}} = -0.60\text{ V}$, but it is at least one order of magnitude smaller than in the previous case.

The observed dependences of SERS signal on the potential of electrode are caused by processes which occur on the electrode surface [13]. For potentials at which the current is positive, the oxidation of the electrode ($\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$) occurs and Ag surface becomes partially covered by AgCl layer. Next, when the current becomes negative, the reduction of AgCl layer ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$) begins. The reduced Ag^0 atoms and the clusters of Ag^0 atoms which play the role of adatoms are surrounded and immobilized by the adsorbed chloride anions, water and pyridine molecules. We assume that complexes of adatom-adsorbed molecule (adatom-adsorbate) are formed on the surface. During the reduction process the number of adatoms increases and, as it is shown in Fig. 1, the SERS signal increases as well. The maximum of SERS signal is reached at the potential equal to $V_{\text{SCE}} = -0.60\text{ V}$. At this potential the number of adatoms as well as the number of adsorbed pyridine molecules on the surface are maximal. We also believe that at this potential the number of complexes of adatom-adsorbed pyridine molecule is maximal. During the decrease of the potential toward more negative one the Cl^- anions and molecules are desorbed, the dissociation of adatom-adsorbate complexes occurs, which allows the Ag^0 adatoms to diffuse and to be incorporated into the solid metal. As a consequence of desorption and absence of adatoms the SERS signal decreases and becomes undetectable at $V_{\text{SCE}} = -1.20\text{ V}$. For less negative potentials, the pyridine molecules are readsorbed, but the number of Ag^0 adatoms becomes small and therefore the SERS signal recorded when the potential increases is much lower than that for the opposite potential sweep. To obtain again the strong SERS signal one has to increase the number of adatoms by the next oxidation and reduction cycle.

Voltammograms and voltammograms presented in Figure 1 were recorded during one OR cycle. These characteristics in Fig. 1a were recorded for slightly oxidized electrode (small current of oxidation and small current of reduction). Figure 1b presents the same dependences for the case of stronger oxidation of the electrode (oxidation potential limit is equal to +0.30 V). Voltammograms shown in Fig. 1a and 1b have different shapes. The reduction process of a strongly oxidized surface needs longer time than that for weakly oxidized. Therefore, for strongly oxidized surface a large SERS signal appears for the lower potential,

as compared to the weakly oxidized one. However, for potentials, at which the electrode is totally reduced, these dependences are nearly the same.

The observed dependences of SERS signal on the electrode potential are caused by the change of adatom concentration on the surface, *i.e.* by the change of atomic roughness. It proves that, the atomic scale roughness has an essential influence on the SERS signal intensity. These dependences of SERS signal on the electrode potential, and consequently on the adatom or adatom-adsorbate concentration, may confirm the existence of chemical mechanism of enhancement in SERS.

3.2. SERS intensity dependence on electrode temperature

In the previous part of the paper, we demonstrated that in a certain range of electrode potentials the adatom-adsorbate complexes are formed, while in another range of potentials they are destroyed. The concentration of adatom-adsorbate complexes and consequently the value of SERS signal may be also changed by the variation of the electrode temperature. The influence of temperature on the SERS signal was discussed in [14]–[17]. The results of our investigations are presented below.

The electrode was initially activated by 3 ORC in the range of $V_{\text{SCE}} = -1.20 - +0.30$ V. The strongest SERS band of pyridine (1008 cm^{-1}) was used. The potential of the electrode during the measurements was kept equal to -0.6 V, while its temperature was altered at the rate of 2 K/min starting from room temperature up to 383 K and back again. SERS intensity measurements during temperature variation were carried out in short periods of time in which the electrode was illuminated by laser light. Results of these measurements are shown in Fig. 2. One can see that the SERS signal decreases as the temperature rises. For the temperatures above 313 K , one may observe a particularly rapid lowering

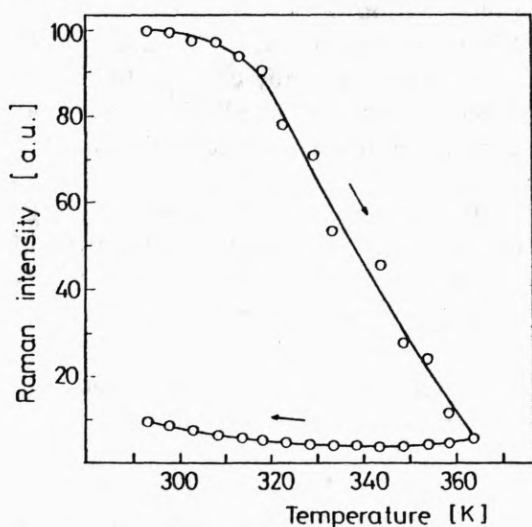


Fig. 2. SERS intensity of 1008 cm^{-1} band of pyridine adsorbed onto Ag electrode vs. electrode temperature

of the SERS intensity. When the temperature of the electrode reached 363 K, it was then decreased. SERS signal initially continued to decrease, but at much lower rate. For temperatures below 333 K, the SERS signal started slightly to increase. At room temperature the SERS signal did not attain the initial value and was at least one order of magnitude smaller than that before the heating process. To obtain again the same SERS signal as observed at the beginning of temperature changes, at least one oxidation-reduction cycle had to be applied.

From our previous considerations, it follows that the concentration of adatom-adsorbate complexes has an essential influence on the intensity of SERS signal. We suppose that the decrease of SERS signal with temperature increase is caused by the loss of adatom-adsorbate complexes on the surface. The increase of temperature causes the decomposition of these complexes and in consequence adatoms are irreversibly incorporated into the electrode, while the molecules are partially desorbed. The temperatures from the range 363–333 K (during the decrease of temperature) are still sufficiently high for decomposition process. The slight increase of the SERS signal for temperatures below 333 K may be explained by readsorption of the previously desorbed molecules.

From comparison of Figures 1 and 2, one can see that in the process of temperature variation from room temperature to 363 K and inversely the SERS intensity behaves in the same way as during the electrode potential variation from -0.60 V to -1.20 V and inversely. The irreversible dependence of SERS intensity on temperature is caused by irreversible loss of adatoms at high temperatures.

3.3. SERS intensity dependence on time and illumination

The phenomenon of decrease of SERS intensity with time, which passed after termination of ORC procedure, was observed by several authors [18]–[23]. On the other hand, the influence of the electrode illumination during ORC on the SERS signal has also been investigated [24]–[26]. It was found that the illumination of electrode by strong laser light during the entire ORC radically enlarges the SERS signal. This is known as illumination effect. Variations of SERS intensity as a function of time, which passed after the termination of electrode reduction, are the subject of our investigations described below.

Ag electrode was initially activated by 3 ORC for the potential sweep in the range from -1.20 to $+0.30$ V. During entire ORC it was illuminated by laser light of 200 mW. The SERS intensity of 1008 cm^{-1} pyridine band at $V_{\text{SCE}} = -0.60$ V was measured as a function of time at room temperature. The measurements were performed for two cases:

- i) without illumination of the electrode (laser light fell on the electrode only during short periods of time necessary to record SERS signal intensity),
- ii) with permanent illumination of the electrode.

The results of these measurements are presented in Figure 3. The dashed line curve presents results obtained for the first case. The dependence of SERS signal on time for the case of illuminated electrode is represented by the solid line curve. One can find that the SERS signal decreases with time in both cases and that the

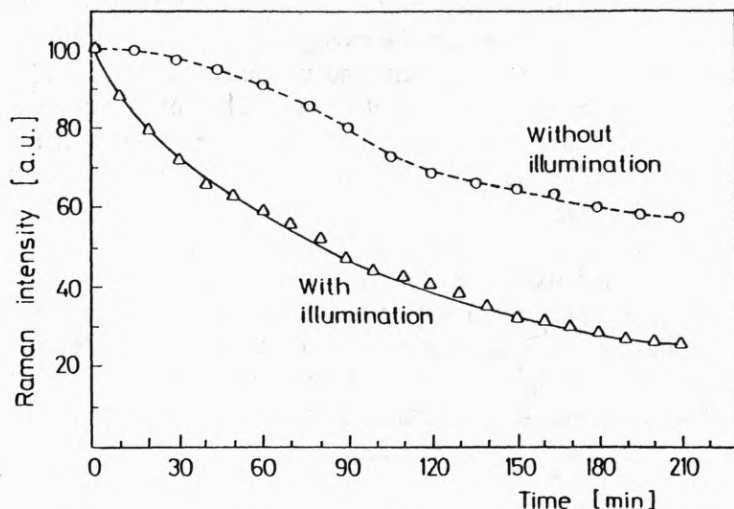


Fig. 3. Dependence of SERS intensity of 1008 cm^{-1} band of pyridine adsorbed onto Ag surface on time for the nonilluminated and illuminated electrode. The power of 514.5 nm laser line illuminating the electrode was equal to 200 mW

illumination has an essential influence on the rate of SERS intensity decrease. The SERS intensity decreases faster for the permanently illuminated electrode. After 1 h the SERS intensity for the illuminated electrode decreases to about 60% of its initial value, whereas for the nonilluminated one only to about 90%. After 3.5 h SERS signal decreases to about 25% and 60% of initial value for the illuminated and nonilluminated electrode, respectively. One can observe that in the case of electrode permanently illuminated, the illumination of previously nonilluminated fragment causes the increase of SERS intensity to the value which corresponds to that for nonilluminated electrode.

On the basis of the obtained results, we propose the following explanation. The decrease of SERS signal with time is caused by decrease of adatom concentration on the electrode surface. This is an effect of the decomposition of adatom-adsorbate complexes caused by thermal motion, which leads to the loss of adatoms. Illumination of the electrode accelerates the decomposition process. It is caused by local laser heating of electrode [21] (the process of thermal-decomposition of adatom-adsorbate complexes is then accelerated) as well as by the additional photo-decomposition of adatom-adsorbate complexes. The faster decrease of SERS signal on the illuminated electrode compared to the nonilluminated one is then caused by both thermal- and photo-decomposition processes.

3.4. SERS intensity dependence on micro-roughness

In previous sections we discussed how changes of the electrode potential after termination of the reduction process, temperature increase, illumination and time, influence the SERS signal. These parameters alter the atomic scale roughness, but do not change the micro-roughness. The micro-roughness may be altered by the change

of parameters of ORC. The investigations performed in our previous work [12] proved that the value of SERS signal depends on the sweep rate of potential during ORCs. In that work the electrode potential was changed in the range from -1.20 to $+0.15$ V with three different sweep rates: 50, 5 and 1 mV/s. The authors noticed that the electrode subjected to very fast OC procedure provides the smallest SERS signal, subjecting to the slowest OC procedure leads to the largest one. It seems that, if the sweep rate during OR cycle is small, the micro-roughness with optimum size for SERS phenomenon is formed. We present here the results of investigations of the SERS signal dependences on the oxidation potential limit in ORC and on the number of ORC. The ORCs were performed with 5 mV/s sweep rate. The SERS intensity of 1008 cm^{-1} pyridine band was measured at -0.6 V electrode potential. The electrode was illuminated by laser light during the whole experiment. Results of these investigations are shown in Fig. 4. One can see that:

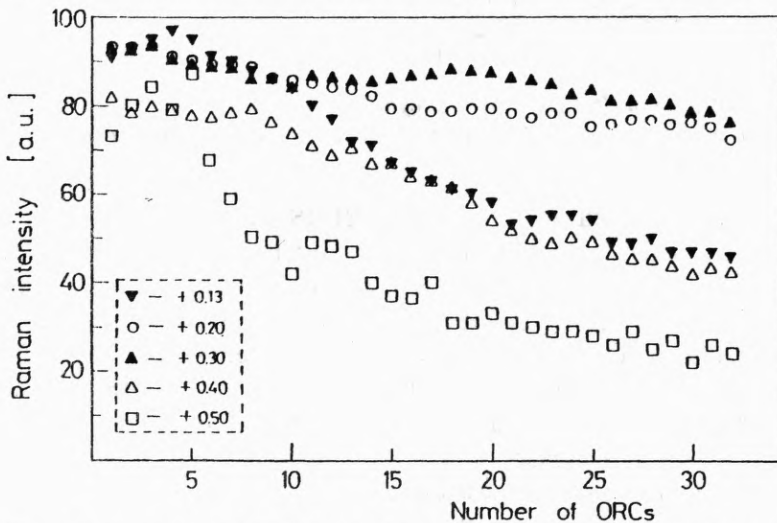


Fig. 4. Dependence of SERS signal of the 1008 cm^{-1} band of pyridine on the number of OR cycles for electrodes oxidized during OR processes to the following oxidation potential limits: 0.13, 0.20, 0.30, 0.40 and 0.50 V. The potential sweep rate during ORCs was equal to 5 mV/s

1. If the electrode is weakly oxidized (oxidation potential limit equal to $+0.13$ V), the maximal value of SERS signal is observed after 3 ORCs.
2. The increase of oxidation potential limit causes that the maximal SERS signal is already observed after one ORC cycle.
3. The SERS signal decreases as the number of ORCs increases. The smallest decrease of SERS signal with the increase of ORC number was observed for the oxidation potential limits equal to $+0.20$ and $+0.30$ V.
4. The strongly oxidized (oxidation potential limits equal to $+0.40$ and $+0.50$ V) and next reduced surfaces give the large SERS signal after one OR cycle, but this signal decreases fast as the number of ORCs increases. Weakly oxidized surfaces (oxidation potential limit equal to $+0.13$ V) after few ORCs behave similarly to those strongly oxidized.

After 32 ORCs and SERS measurements each electrode considered here was taken out from the electrochemical cell, washed and dried and next its roughness was tested by angle distribution measurements of the elastically scattered laser light. The results of these measurements are presented in Fig. 5. From comparison of Figs. 4 and 5, it follows that the optimal SERS signal occurs only in a particular range of micro-roughness. The surfaces weakly oxidized (oxidation potential limit equal to +0.13 V) are still roughened too little, whereas the surfaces oxidized strongly (oxidation potential limit equal to +0.40 V and larger) are already roughened too much. It seems most likely that the roughness of electrodes, which were oxidized with the use of potential limit equal to +0.20 and +0.30 V, respectively, is most appropriate. Electrodes oxidized with these potential limits show the largest signal after one OR cycle and the value of this signal only weakly decreases as the number of ORC increases.

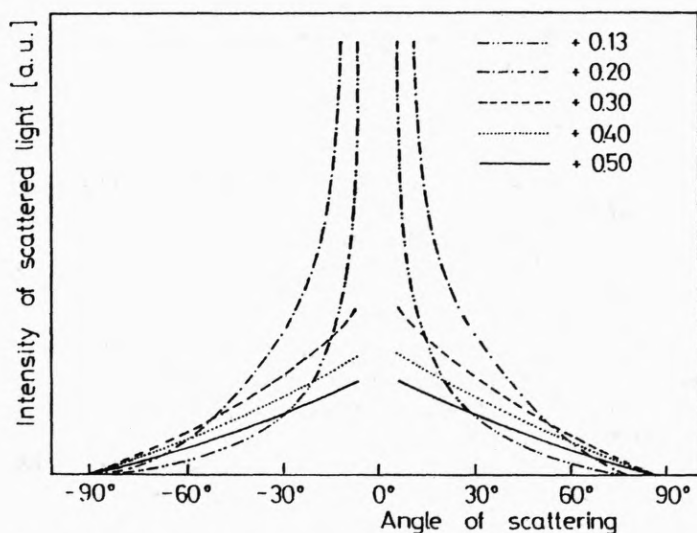


Fig. 5. Angle distribution of elastically scattered laser light intensity on the silver electrode. Each investigated electrode was roughened by 32 ORCs using in OR processes the following oxidation potential limits: 0.13, 0.20, 0.30, 0.40 and 0.50 V

The presented dependences of SERS signal and micro-roughness on the oxidation potential limit in ORC prove that the micro-roughness has an essential influence on the value of SERS signal. From the performed investigations it follows that the large SERS signal is obtained only for the surfaces of appropriate roughness. The CEME model predicts that the existence of small and prolate micro-structures is necessary for large enhancement. We suppose that the small micro-structures exist only on the reduced surface which has been previously weakly oxidized. Increase of the oxidation potential limit causes the prolongation of these micro-structures. Continuation of the increase of the oxidation potential limit and increase of ORC number leads to the formation of larger and larger micro-structures. This leads to the decrease of SERS signal.

4. Conclusions

The SERS signal from pyridine molecules adsorbed on the silver electrode was investigated. We found that the SERS signal intensity is determined by the electrode potential and its sweep direction, temperature, illumination and the time passed after the termination of the reduction process. Changes of the above mentioned parameters alter the concentration of the adatom-adsorbate complexes and in consequence lead to the change of SERS intensity. Sensibility of the SERS intensity on the change of adatom-adsorbate concentration well proves the existence of the chemical enhancement mechanism in the SERS phenomenon.

On the other hand, the dependence of the SERS intensity on the type of ORC realization and in consequence on electrode micro-roughness proves the existence of CEME mechanism. According to the prediction of CEME model, we observed that the largest SERS signal occurs for the small and prolate micro-structures.

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