Spectroscopic study of SERS- and SEIRA-activity of copper large-scaled surface substrates prepared by electrochemical deposition: What is the role of oxidation–reduction cycle treatment?

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ABSTRACT

Surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) are powerful analytical techniques used for the study and characterization of ultrathin films and monolayers of organic compounds adsorbed on the nanostructured surface of several metals. The main requirement which has to be met for the SERS- and SEIRA-activity is the proper morphology of the surface in nanoscale, which can be tailored by the preparation procedure.

In the present work different electrochemical preparation procedures of copper substrates (cathodic reduction from electrochemical baths or its combination with oxidation–reduction cycles (ORC) treatment) were developed with the aim of fabrication of the substrate with both SERS- and SEIRA-activity for the selected model analyte. The diffuse reflectance methodology was designed to study SEIRA-activity on large-scaled nanostructured surfaces. The nanostructure of the copper surface was characterized using Scanning Electron Microscopy (SEM). The effect of different ORC treatments on the surface morphology as well as on SERS- and SEIRA-activity is discussed. The interpretation of SERS and SEIRA spectra has been made in terms of the comparison of these two types of surface-enhanced spectra with normal infrared and Raman spectra and DFT calculation elucidating the orientation of the molecule on the surface.

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1. Introduction

Films and monolayers of organic compounds on several metal surfaces are widely studied and analyzed by surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) spectroscopy considering significantly increased sensitivity of these techniques with respect to their normal (non-enhanced) counterparts. Taking into account the fact that SERS and SEIRA (the same as normal Raman and infrared spectroscopy) are the two faces of the vibrational coin, there is a big advantage of combination of these two techniques over their particular use, due to the complementarity of data obtained. SERS, as a short-range effect, has been shown to be usually the most sensitive to the first adsorbed monolayer [1–3]. On the other hand, SEIRA is a longer-range effect, which can provide frequently the enhancement of both the monolayer and multilayer [4–7].

SERS phenomenon is based on the enhancement of Raman signal of the molecules localized in the close proximity of the nanostructured surface of certain (SERS-active) metals. This extremely high enhancement (generally 10^5–10^6 in some cases up to 10^{14}) is caused predominantly by collective resonance excitation of localized conduction electrons (called surface plasmon modes) on the nanostructured features of metal surface. Optically excited surface plasmons can be considered as oscillating dipoles, which emit enhanced electromagnetic radiation of the same wavelengths as the incident one [8–11]. This local enhanced electromagnetic field generates Raman scattering in the molecules situated on the nanofeatures of the surface. This process is the fundamental of so called electromagnetic enhancement (EM) mechanism of SERS and it is a direct consequence of the roughened nanostructure on a metal surface. The other, so called chemical mechanism (CM), which has to be considered, involves changes of the adsorbed molecules electronic states caused by the chemisorption of the analyte and provides an order or two of magnitude enhancement to the overall Raman signal intensity [12–15]. In the case of SEIRA the electromagnetic enhancement is believed to play the most substantial role, absorption of infrared radiation in SEIRA measurements can be enhanced in two or three orders in absorbance scale [16,17]. Both SERS and SEIRA found their EM mechanism origin in a light interaction with nanoparticles/nanostructures. SERS is observed primarily for analytes adsorbed onto the surface of coinage

(Au, Ag, and Cu) metals [18–20], because they match very well the (plasmon) resonance condition and are able to give efficient SERS effect in visible and/or near-infrared range. Commonly, the same active rough surface which is used in SERS experiments may also be used for SEIRA. In particular, mentioned above coinage metals, have also been widely employed for SEIRA measurements [8,17,21].

It is well-known that one of the most important factors which influence the ability of the substrate to be SERS- or SEIRA-active is the morphology of its surface in nanoscale [11,22]. As far as the surface properties can be modified by changing the conditions of preparation procedure, it is obvious, that one of the main challenges in substrate preparation is the modification and optimization of all conditions of substrate fabrication procedure in terms of achieving the nanomorphology, which produces the best enhancement of Raman scattering and/or infrared absorption signal of detected substances. From this point of view it is very important to monitor the structure and shape of all nanofeatures on the surface and their relations to signal enhancements.

There are various procedures how to prepare SERS-active substrate: vacuum thermal evaporation of metal particles [23–25], reduction of metal salts with various chemicals producing nanoparticles [26–29], sol–gel process [30,31], coating of inert metal surfaces by cathodic reduction [32,33] or oxidation–reduction cycling (ORC) on a metal electrodes [14,34]. Some of these procedures require expensive instrumentation. The last two mentioned techniques can be suitably combined: substrate surface formed by cathodic reduction is subsequently appropriately roughened by ORC treatment procedure. This combination can give rise to the substrate surface with better SERS/SEIRA-activity (ability of signal enhancement). In general, the optimum roughness of substrate surface, which is responsible for enhancement of Raman or infrared signal, is dependent mainly on the cathodic and anodic scan rates and vertex potentials, duration time at each vertex and number of cycles and on the type of electrolyte used.

The aim of this work is: (i) development of appropriate combined electrochemical preparation procedures of copper substrates using the cathodic reduction from electrochemical baths with oxidation–reduction cycles treatment to achieve high level of SERS- and SEIRA-activity of prepared substrates and (ii) elucidation of detailed structural architecture of the model analyte (4-aminobenzenethiol)/Cu substrate system profiting from the combination of SERS and SEIRA data measured on the same samples and further comparison with normal vibrational spectra and results of density-functional theory calculations. We compare the results of spectroscopic measurements on the substrates prepared from both acidic and ammoniac bath either by bare cathodic reduction or cathodic reduction and subsequent ORC treatment with different conditions in order to describe the influence of subsequent changes of surface morphology (monitored by SEM) on SERS- and SEIRA-activity both from the point of view of signal intensity and possible variation of surface geometry of the model analyte. The results of principal component analysis of spectral data elucidate the relatively minor role of ORC treatments compared to crucial effect of conditions of cathodic reduction.

2. Experimental

2.1. SERS-active substrates preparation

All experiments were performed on massive platinum targets (diameter 10 mm, thickness 2 mm, Safina, Czech Republic), which were coated by copper layer using electrochemical procedures. After the polishing and pretreatment of platinum targets, described elsewhere [35], the electrochemical procedure of copper deposi-

tion followed. All procedures were performed in the electrochemical cell, where flat copper electrode was used as anode and platinum target was a cathode. Copper coating was performed either from an acidic ($CuSO_4/H_2SO_4$) bath or an ammoniac ($[Cu(NH_3)_4]SO_4$) bath in order to monitor the influence of bath composition on the nanomorphology of the surface. Conditions of cathodic reduction for each of the bathes including the current values applied in each step were selected on the basis of our previous study [35] and they are described in Table 1. The preparation procedures and composition of bathes used were described previously [35]. After the coating, every substrate was taken out of the cell and thoroughly rinsed with diluted sulfuric acid (1:4 v/v) and redistilled water repeatedly. To study the effect of modification of surface morphology on surface enhancement (both SERS and SEIRA), the procedure of copper coating was followed by various ORC treatments (Table 2).

ORC procedures were carried out in a typical 3-electrode potentiostatic system. The copper coated target was used as working electrode, a platinum sheet as the counter electrode and a saturated silver/silver chloride (Ag/AgCl) as the reference. All potentials are reported with the respect to Ag/AgCl electrode. ORC treatment procedures were carried out in three different electrolyte solutions: (i) 0.1 M KI (E1), (ii) 0.1 M KCl (E2), and (iii) mixture of 0.2 M LiCl and 0.01 M $CuCl_2$ (E3). Before initiation of the procedure electrolyte solution was bubbled with nitrogen. After the subjection of the last cycle the substrate was taken out of the cell and thoroughly rinsed with diluted sulfuric acid (1:4 v/v) and redistilled water and methanol repeatedly and dried in nitrogen flow. Before the deposition of model analyte the substrate was stored in methanol (analytical grade) to prevent sorption/corrosion processes on its surface. Potential ranges, number of scans and scan rates applied within the four types of ORC treatments are summarized in Table 2. All combined preparation procedures (AORC1, BORC1, etc.) are denoted by combination of labels used for the type of electrochemical coating bath (A or B – Table 1) and labels for ORC treatment procedure (Table 2).

2.2. Deposition of model analyte

In this study 4-aminobenzenethiol (4-ABT) (Fluka) was used for evaluation of SERS- and SEIRA-activity of copper substrates. All deposition procedures were performed from 1 mM solutions of 4-ABT in methanol. Individually fabricated copper substrate was immersed into the glass vial with 4 ml of sample solution, usually for 20 h. Afterwards the target was taken out of the solution and rinsed with methanol (to remove physisorbed molecules of the analyte) and redistilled water repeatedly. Finally, the modified target was dried in N_2 flow.

2.3. Spectral measurements

Raman spectra were collected using a disperse Raman (micro)spectrometer LabRam (Dilor Jobin–Yvon, France), which was equipped with microscopic objectives (magnification: 10×,

Table 1
Conditions of electrochemical copper coating procedures.

Acidic bath (A)		Ammoniac bath (B)	
Current (mA)	Time (s)	Current (mA)	Time (s)
5	20	10	10
10	10	20	10
15	10	30	10
20	5	40	10
		50	10
		60	10