Raman spectroelectrochemical study of electrodeposited Prussian blue layer: dependence of spectral intensity on underlying electrode roughness

Regina Mažeikienė,

Gediminas Niaura,

Albertas Malinauskas*

Institute of Chemistry,
Center for Physical Sciences and Technology,
Saulėtekio Ave. 3,
LT-10257 Vilnius, Lithuania

Prussian blue (PB) has been electrodeposited at a smooth and at an electrochemically roughened gold electrodes as a thin layer of a few tens of nmol/cm^2 coverage (or a few tens of nanometers thick), and studied by Raman spectroelectrochemical technique using 785-nm laser excitation. It has been shown that the spectra obtained from a roughened electrode are by one order of magnitude more intense than those obtained from a smooth electrode. This shows that even at a relative thick layer of a modifier PB the surface enhancement of Raman spectra plays an important role in obtaining well-defined spectra from modified electrodes.

Keywords: Raman spectroscopy, spectroelectrochemistry, modified electrode, Prussian blue

INTRODUCTION

Surface enhanced Raman scattering (SERS) is an important phenomenon, widely applied in different fields of research and technology [1]. Localised surface plasmon resonance as a response to optical excitation by visible and near infrared light has been known long ago. As a result of this resonance, strong electromagnetic fields are generated, and the intensity of inelastic Raman scattering from molecules present at a nanostructurized noble metal surface is highly increased. A total enhancement ranging from 10^5 to 10^{14} can be obtained [1].

Many efforts have been made through decades to create SERS-active structures capable to enhance Raman scattering from adsorbed molecules or particles. In particular, noble metal nanoparticles as plasmonic nanosensors possessing extremely high enhancement, even reaching a single molecule detection level, are widely used and well reviewed [2–4]. Also, e-beam lithography and related techniques are used to obtain repeatable sensitive substrates [5, 6]. Morphological diversity of silver nanomaterials has been shown to highly influence sensitive and selective detection schemes based on SERS [7].

It is well known that the most intense Raman scattering is obtained from the nearest layer of adsorbate adjacent to the nanostructured interface. For electrochemical applications, like sensors, batteries or electrocatalytic systems, however, much thicker layers of electrode modifiers are often used. Then, the problem is whether the data obtained by Raman spectroscopy, especially by SERS, relate to a thin, even a monomolecular layer at the electrode surface, or to a thicker one? Or: How does Raman scattering from a monolayer of adsorbate compete with that from the bulk of the modifier layer? Previously, for relatively thin layers of adsorbed azine type dyes Toluidine blue [8] or Neutral red [9] we obtained Raman spectra closely related to those from electropolymerized layers of these species. In this case, however, electropolymerized layers do not differ significantly by their thickness from adsorbed layers. A different situation would be observed for thicker layers of an electrode modifier, like e. g. transition metal hexacyanoferrate complexes, often used for electrocatalytic sensors and biosensors [10, 11]. In such cases, the main question is as follows: Do the spectral features and their changes observed relate to a thin layer nearest to the electrode surface, or to an entire thick layer of a modifier at the electrode? There should be many theoretical aspects of this important problem, however, our present study has been aimed at more practically related aspects. In the present study, we concerned about Prussian blue (ferrous hexacyanoferrate) modified electrode, well known and widely applied in electrocatalysis and electroanalytical systems.

* Corresponding author. E-mail: albertas.malinauskas@ftmc.lt

EXPERIMENTAL

A BASi-Epsilon model potentiostat (Bioanalytical Systems Inc., USA) was used in electrochemical experiments. As a working electrode, a flat circular gold electrode of 5 mm in diameter, press-fitted into a Teflon holder, was used. Platinum wire, as a counter electrode, and a KCl saturated Ag/AgCl reference electrode were used to accomplish an electrochemical circuit. All potential values reported below refer to this reference electrode. Commercially available analytical or reagent grade chemicals were used as received.

The electrode preparation procedure consisted of etching for 1 h in a Piranha solution (a mixture of 30% hydrogen peroxide and sulfuric acid, approx. 3:1 by volume), and the next following cleaning by ultrasonication for 2 min in ethanol and water mixture. Following this way, a clean smooth electrode was prepared, designed below as an Au electrode. For preparation of a roughened SERS active electrode (designed below as Au(SERS) electrode), the Au electrode was additionally electrochemically roughened in a 0.1 M solution of KCl by potential cycling for 50 cycles within the limits of −0.3 and 1.4 V at a scan rate of 0.2 V/s. The deposition of a Prussian blue layer onto the Au or Au(SERS) working electrode has been performed in a freshly prepared solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM $K_3[Fe(CN)_6]$, and 2.5 mM $FeCl_3$ (pH 0.95) by applying a controlled potential of 0.4 V for 1 min. After that, the electrode was rinsed with water and transferred into a background electrolyte containing 0.1 M KH_2PO_4 and 0.1 M KCl (pH 5.4). All spectroelectrochemical experiments were done in this background electrolyte.

Raman spectroelectrochemical experiments were done in a cylinder-shaped three electrode cell, equipped with a gold working electrode (as indicated above), a platinum wire counter electrode, and a KCl saturated Ag/AgCl reference electrode. Raman spectra were recorded using an Echelle type spectrometer RamanFlex 400 (PerkinElmer, Inc.) equipped with a thermoelectrically cooled up to −50 °C CCD camera and a fiber-optic cable for excitation and collection of the Raman spectra. The 785-nm beam of the diode laser was used as the excitation source. The 180° scattering geometry was employed. The laser power at the sample was restricted to 30 mW and the beam was focused to a 0.2 mm diameter spot on the electrode. The integration time was 100 s. The working electrode was placed at approx. 3 mm distance from the cell window. In order to reduce photo- and thermoeffects, and a possible degradation of the Prussian blue film by the incident light as well, the cell holder was moved periodically with respect to the laser beam at ca. 15–25 mm/s with the help of custom built equipment [12].

RESULTS AND DISCUSSION

Figure 1 compares the cyclic voltammograms for two Prussian blue (PB) modified electrodes – a smooth cleaned gold
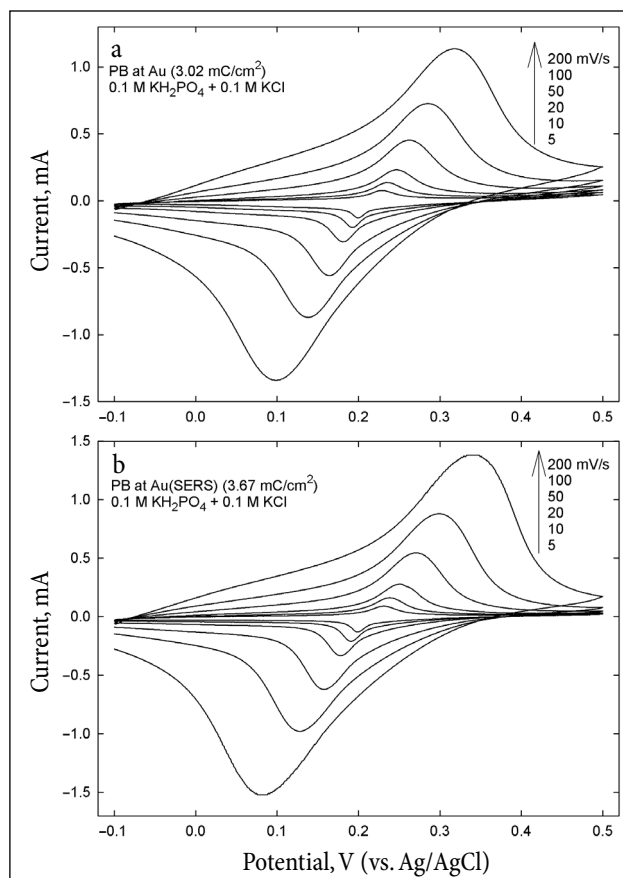

Fig. 1. Cyclic voltammograms of Prussian blue modified Au (a, at the top) and Au(SERS) (b, at the bottom) electrodes, as obtained in an electrolyte containing 0.1 M of KH_2PO_4 and 0.1 M of KCl within the potential scan limits of −0.1 to 0.5 V at different potential scan rate ranging from 5 to 200 mV/s (as indicated)

electrode, and a rougnened, prepared for SERS studies gold electrode. For both electrodes, the well defined anodic and cathodic peaks are observed. Within an entire potential scan rate range studied the peak pairs show a clearly defined separation on the potential scale ranging from 0.03 V at the lowest scan rate of 5 mV/s to 0.22 or 0.26 V at the fastest scan of 200 mV/s for PB/Au and PB/Au(SERS) electrodes, respectively. Taking into account that both anodic and cathodic peaks are obtained from the surface-bound PB layers, it could be concluded that the rate of the electrochemical redox process is controlled by the diffusion of some species through the PB layer, most probably potassium ions according to the equation:

$$Fe_{(N)4}^{III}[Fe_{(C)}^{II}(CN)_6]_3 + 4e^- + 4K^+ \leftrightarrow K_4Fe_{(N)4}^{II}[Fe_{(C)}^{II}(CN)_6]_3.$$
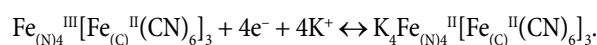
Here $Fe_{(N)}$ and $Fe_{(C)}$ represent Fe ions, coordinated either to N (high-spin Fe ions), or to C (low-spin Fe ions) atoms, respectively.

Also, the closely related midpotential $(E_{pa} + E_{pc})/2$ values were obtained for both types of electrodes. For the PB/Au electrode, midpotential values of 0.215 and 0.210 V were obtained for a potential scan rate of 5 and 200 mV/s,

respectively, whereas values of 0.214 and 0.211 V were obtained for the PB/Au(SERS) electrode, respectively. The obtained values coincide within the error limits with those reported previously [10].

A linear dependence of the peak potential and peak current for both electrodes on the square rooth of the potential scan rate was obtained, as shown in Fig. 2. Extrapolation of the dependence of the peak potential on $v^{1/2}$ to the zero potential scan rate yields again nearly coinciding values of a midpotential of 0.215 V for both types of the modified electrode. A linear dependence of the peak current on $v^{1/2}$, as observed for the cathodic and anodic peaks for both electrodes (Fig. 2), confirms the diffusion-controlled nature of both redox processes.

By integration of anodic and cathodic peak currents, a specific electric charge characteristic of redox processes of both types of the modified electrode could be obtained. For the smooth PB/Au electrode, a mean specific redox charge of 3.02 mC/cm^2 was obtained both from anodic and cathodic peaks, and for all potential scan rate values studied. For the roughened PB/Au(SERS) electrode, a somewhat higher value of a specific charge of 3.67 mC/cm^2 was calculated. Probably, this higher redox capacity of the latter electrode corresponds to somewhat higher surface area, obtained by the roughening procedure. Despite of this difference, the re-

dox capacity for both types of the modified electrode appears closely related, indicating nearly equal amounts of Prussian blue deposited during the preparation procedure. The results presented are well reproducible during the repeated preparation of modified electrodes. Based on the redox charge observed, the mean thickness of the PB layer, as well as the mean coverage could be calculated. As for electrochemically prepared PB layers, it is well known that a redox charge of 5 mC/cm^2 corresponds to 100 nm of layer thickness [13]. Therefore, it could be calculated that the thickness of the PB layer of 60 and 73 nm is characteristic of the prepared PB/Au and PB/Au(SERS) electrodes, respectively. Alternatively, turning to the molar coverage of PB modified electrodes, the values of 31 and 38 nmol/cm^2 can be obtained for the PB/Au and PB/Au(SERS) electrodes, respectively. It could be concluded that nanometer-sized well-reproducible PB layers containing a few tens of nanomoles of PB per cm^2 were prepared by the electrodeposition procedure applied for both smooth and roughened gold electrodes.

The electrodes prepared were subjected to a combined Raman electrochemical study. Figure 3 shows the characteristic Raman spectra, obtained from the smooth PB/Au electrode. Two different redox forms of PB are well discernible. At the applied potential of 0.1 V, the reduced form of PB, *viz.* Prussian white (PW), prevails. Within the most characteristic Raman spectral range of 2200–2000 cm^{-1}, stretching vibrations of the triple C–N bonds are observed. Different frequencies of C–N bond stretchings are caused by a different valence state of the Fe ions, to which the CN ligands are coordinated. For PW, the presence of a characteristic frag-
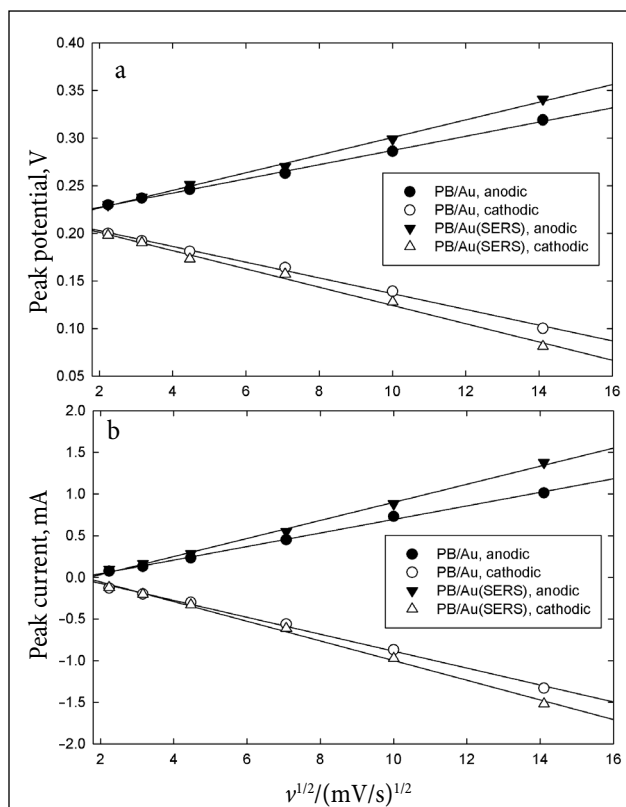

Fig. 2. Dependence of the peak potential (a, at the top) and peak potential (b, at the bottom) on the square rooth of potential scan rate, as obtained for the cathodic and anodic peaks of Prussian blue modified Au and Au(SERS) electrodes (as indicated)
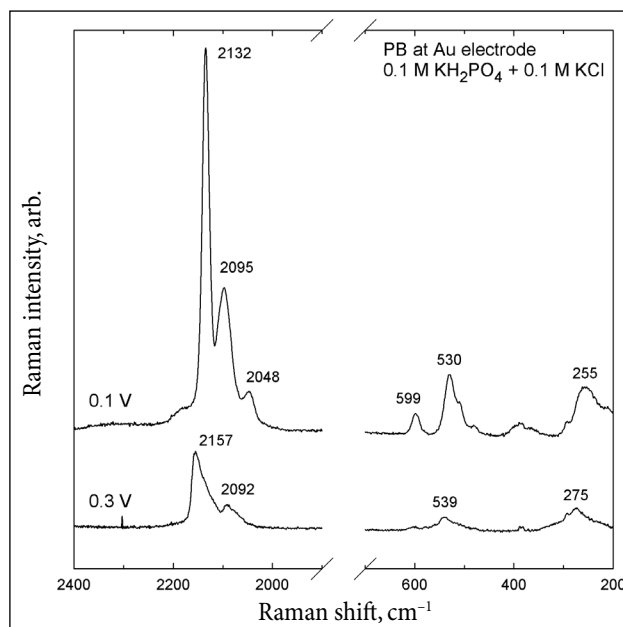

Fig. 3. Raman spectra, presented within wavenumber ranges of 2400–1900 and 700–200 cm^{-1}, from the Prussian blue modified Au electrode, obtained in a solution containing 0.1 M of KH$_2$PO$_4$ and 0.1 M of KCl using 785 nm laser excitation at electrode potential of 0.1 and 0.3 V (as indicated)

ment Fe^{II}–CN–Fe^{II} results in three Raman bands within this region: a strong band centered at 2132 cm^{-1}, a mid-intense band at 2095 cm^{-1}, and a weak band at 2048 cm^{-1}. Within the lower frequency range, the well-defined mid-intense bands observed at 599 and 530 cm^{-1} (and probably some other low-intense bands within this range) correspond most probably to the Fe–C stretching vibrations, and the band at 255 cm^{-1} corresponds to the deformation vibrations of Fe–C–N fragments [14]. At the applied potential of 0.3 V, the oxidised form of PB prevails. Within a high frequency range, a mid-intense band located at 2157 cm^{-1}, and a weak band at 2092 cm^{-1} are observed (Fig. 3). Also, changes within the low-frequency range are evident by turning from PW to PB. The intensity of Raman bands for PB appears lower than for PW (Fig. 3).

Nearly same results regarding Raman band frequencies were obtained from both PB/Au and PB/Au(SERS) electrodes, except for some minor bands within the low-frequency range. However, a drastic difference in spectral intensity was observed for these two types of electrodes, as depicted in Fig. 4. The spectrum obtained from the PB/Au(SERS) electrode is much more intense than that from the unroughened PB/Au electrode. By integration of band intensities within a range of 2200–2000 cm^{-1}, an enhancement factor of ca. 11 could be obtained for the roughened PB/Au(SERS) electrode. This shows that even at a relative thick layer of a modifier PB, consisting of a few tens of nanometers, or, in other terms, a few tens of nmol/cm^2 for surface coverage by an electrochemically active substance, the surface enhancement of Raman spectra plays an impor-

tant role in obtaining well-defined spectra from modified electrodes. It could be speculated whether the thinnest (or even a monomolecular) layer at the electrode surface or the rest bulk layer add more or less to the net intensity of spectra, however, it is seen that the position of Raman bands as well as their relative intensity ratio do not practically differ for both types of electrodes. From a practical point of view, the results obtained show that even for relative thick modifier layers like those obtained by electrodeposition or electropolymerization procedures, next to monolayers of adsorbate, it is expedient to apply a surface roughening procedure in order to get more intense Raman spectra.

CONCLUSIONS

When deposited at a roughened gold electrode surface, Prussian blue layers show approximately ten times more intense Raman scattering as compared to those layers deposited at a smooth gold electrode. This clearly shows that even for relatively thick modifier layers of a few tens of nanometers, surface Raman enhancement plays an important role.

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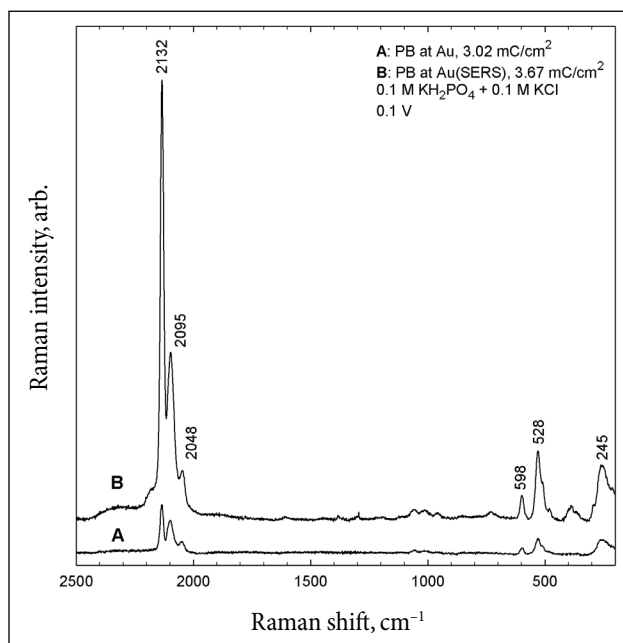14. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1963).

Fig. 4. Raman spectra, presented within a broad wavenumber range of 2500–200 cm^{-1}, from the Prussian blue modified Au and Au(SERS) electrodes (as indicated), as obtained at the electrode potential of 0.1 V

Regina Mažeikienė, Gediminas Niaura, Albertas Malinauskas

ELEKTRONU SODINTO BERLYNO MĖLIO SLUOKSNIO TYRIMAS RAMANO SPEKTROELEKTROCHEMINIU METODU: ELEKTRODO ŠIURKŠTUMO ĮTAKA SPEKTRŲ INTENSYVUMUI

Santrauka

Ploni Berlyno mėlio sluoksniai elektrocheminiu būdu nusodinti ant lygaus ir elektrochemiškai šiurkštinto aukso elektrodo paviršių. Gautieji sluoksniai, kurių storis sudaro kelias dešimtis $nmol/cm^2$ (arba kelias dešimtis nanometrų), buvo tiriami Ramano spektro-elektrochemijos metodu, taikant 785 nm bangos ilgio spektro su-žadinimą. Nustatyta, kad spektrai, gauti nuo šiurkštinto elektrodo paviršiaus, yra maždaug viena eile intensyvesni nei spektrai, gauti nuo lygaus elektrodo paviršiaus. Prieita prie išvados, kad, net esant gana storam elektrodo padengimui Berlyno mėlio sluoksniu, pavir-šiaus stiprinimas yra svarbus veiksnys, lemiantis bendrą Ramano spektro intensyvumą.