



# Raman spectroelectrochemical study of electrode processes at hybrid polyaniline - copper hexacyanoferrate modified electrode



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## ABSTRACT

Electrochemical redox processes taking place within a hybrid polyaniline (PANI) and copper hexacyanoferrate (CuHCF) modified electrode, as well as of solution species at the surface of a modified electrode, have been investigated by near-infrared laser (785 nm) induced Raman spectroscopy. It has been shown that the composite CuHCF-PANI layers can be obtained at electrode surface by first covering the electrode by CuHCF layer using potential cycling procedure, followed by electropolymerization of aniline onto this layer at a controlled electrode potential. A reverse in this order does not result in a composite layer. Raman bands observed within a broad spectral range, as well as their dependence on electrode potential, have been analyzed. Electrochemically driven changes in spectral features related to redox transformations both of PANI and CuHCF have been observed and discussed. Slow redox transformations have been noted, most probably related to slow charge transfer within these hybrid layers. Electrochemical reduction of hydrogen peroxide at a hybrid modified electrode occurs through the redox mediation of CuHCF, whereas PANI remains not involved in this process.

## 1. Introduction

Among many, the two types of materials have been extensively studied as electrode modifiers during recent decades due their promising applications in a wide variety of fields, mostly related to electrochemistry. One of them relates to transition metal hexacyanoferrate complexes. Since the late 70's, when the deposition of Prussian blue layer onto electrode surface has been elaborated [1,2], these modified electrodes have been applied for sensors, biosensors, capacitors, electrochromic devices *etc.* About the same time, or even somewhat later, conducting polymers like polypyrrole and polyaniline have been discovered and studied for possible applications in closely related fields. Later, synergism between these two classes of materials has been disclosed, consisting in an addition or even enhancement of their valuable properties, when they are co-present in composite materials at electrode surface.

This synergism has been exploited in a few different potential fields of application for these materials. One of them relates to sorption of heavy metal ions from industrial wastewater. Cadmium and zinc ions were successfully removed from wastewater using nanocomposites of polyaniline and cobalt hexacyanoferrate (PANI/CoHCF), or polyaniline and zinc oxide (PANI/ZnO) [3]. Similarly, radioactive Cs(I) ions can be removed from nuclear waste by sorption onto a composite PANI/CoHCF [4].

A number of electrochemistry related devices has been proposed with the use of these composite materials. PANI/NiHCF composites were prepared and electrodeposited onto sulfonated carbon nanotubes in one single synthesis step, and the resulting composite has been proposed for supercapacitor application [5]. Similarly, PANI/NiHCF nanogranules have been synthesized and applied for the same purposes [6]. Electrochromic devices are another field for possible applications of these materials. An electrochromic device based on triphenylamine type polymer as electrochromic component, and ZnHCF serving as a storage material exhibiting a high transparency has been proposed [7]. Also, PANI/CoHCF [8], and PANI/InHCF composites [9] have been proposed as an electrochromic materials. It has been shown that a layer order in a composite, covered at electrode surface, plays an important role in electrochromic performance. Inner PANI/outer Prussian blue (PB) configuration has been found to be superior to an adverse configuration in a polyelectrochromic system [10].

Many published works deal with the application of these composites for sensors and biosensors. The ability of a PANI/CuHCF composite covered on a glassy carbon electrode to electrocatalyze anodic oxidation of sulfite has been exploited for an amperometric sulfite sensor, showing a linear range of response at  $4.3 \cdot 10^{-6}$ – $3.9 \cdot 10^{-4}$  M, and a lower detection limit at  $0.6 \cdot 10^{-6}$  M [11]. A high electrocatalytic activity of a composite PANI/NiHCF/carbon nanotubes toward electro-oxidation of ascorbic acid, and thus applicability of this composite in

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amperometric ascorbate sensors has been demonstrated [12]. Traditionally, a high degree of attention has been devoted to amperometric hydrogen peroxide sensors, mainly because their potential use as a components of biosensors in a combination with the peroxide producing enzymes. Hybrid films of PANI/NiHCF have been deposited at carbon nanotubes and used in electrocatalytic amperometric assay of hydrogen peroxide, characterized by a huge range of a linear current response on peroxide concentration at  $1.25 \cdot 10^{-6}$ – $2.95 \cdot 10^{-3}$  M [13]. A high stability and reproducibility of amperometric hydrogen peroxide sensor based on PANI/NiHCF/carbon nanotube composite has been reported [14]. An enhanced sensitivity toward hydrogen peroxide has been noted for polypyrrole/CuHCF composite, when coated over cup-stacked carbon nanotubes grown onto a carbon felt [15]. This material has been used in preparation of glucose biosensor [15].

For successful use of composite materials based on conducting polymers and metal hexacyanoferrates in diverse fields, the knowledge of fundamental peculiarities would be very desirable, related to their properties, composition and structure, as well as mechanisms of charge transfer and electrocatalytic processes taking place with these materials. Raman spectroscopy, especially in a combination with electrochemistry, could be very useful tool for the deep study of processes taking place in these composites. Previously, we studied electrochemical and electrocatalytic redox processes taking place in the deposited layers of Prussian blue [16], CoHCF [17], and CuHCF [18]. The present work has been aimed to Raman spectroelectrochemical study of electrochemical redox processes taking place in a composite layers of polyaniline and CuHCF, deposited at electrode surface.

## 2. Experimental

Commercial available analytical or reagent grade chemicals have been used. BASi-Epsilon model potentiostat (Bioanalytical Systems Inc., USA) has been used in all electrochemical experiments. A flat circular gold electrode of ca. 5 mm in diameter, press-fitted into a Teflon rod, as a working electrode, platinum wire as a counter electrode, and potassium chloride saturated Ag/AgCl reference electrode were used. All potential values reported below refer to this reference electrode.

Before experiments, the working electrode has been cleaned for 1 h in a Piranha solution (a mixture of 30% hydrogen peroxide and concentrated sulfuric acid, 3:1 by vol.), and ultrasonicated for 2 min in ethanol and water mixture. Then, the surface of working electrode has been roughened electrochemically in 0.1 M KCl solution by cycling for 50 cycles within the potential scan limits of  $-0.3$  and  $1.4$  V at a potential scan rate of  $0.2$  V/s.

Two different approaches have been used in obtaining composite CuHCF-PANI films at electrode. For PANI-CuHCF (first polyaniline, then copper hexacyanoferrate layer), the preparation consisted of electropolymerization of aniline and the following electrodeposition of CuHCF. Adversely, for CuHCF-PANI (first copper hexacyanoferrate, then polyaniline layer), first deposition of CuHCF was performed, followed by electropolymerization of aniline. The deposition of a CuHCF layer onto the working electrode has been performed in a freshly prepared solution containing  $0.1$  M of KCl,  $1$  mM of  $K_3Fe(CN)_6$  and  $1$  mM of  $CuCl_2$  by potential cycling within the limits of  $0.0$  to  $0.9$  V at a scan rate of  $0.1$  V/s for different number of cycles ranging from  $5$  to  $50$ . Electropolymerization of aniline has been performed by applying a controlled electrode potential of  $0.8$  V for  $30$  s in a solution containing  $0.05$  M of aniline and  $0.5$  M of sulfuric acid. After that, the modified electrode was rinsed and transferred into a background electrolyte containing  $0.1$  M of KCl and  $0.1$  M of  $KH_2PO_4$ .

The arrangement for Raman spectroscopy was same as in our previous work [18]. Raman spectroelectrochemical experiments have been done in a cylinder-shaped three electrode moving cell, arranged with a gold working electrode (as indicated above), platinum wire counter electrode, and a KCl saturated Ag/AgCl reference electrode. Raman spectra were recorded using Echelle type spectrometer RamanFlex 400

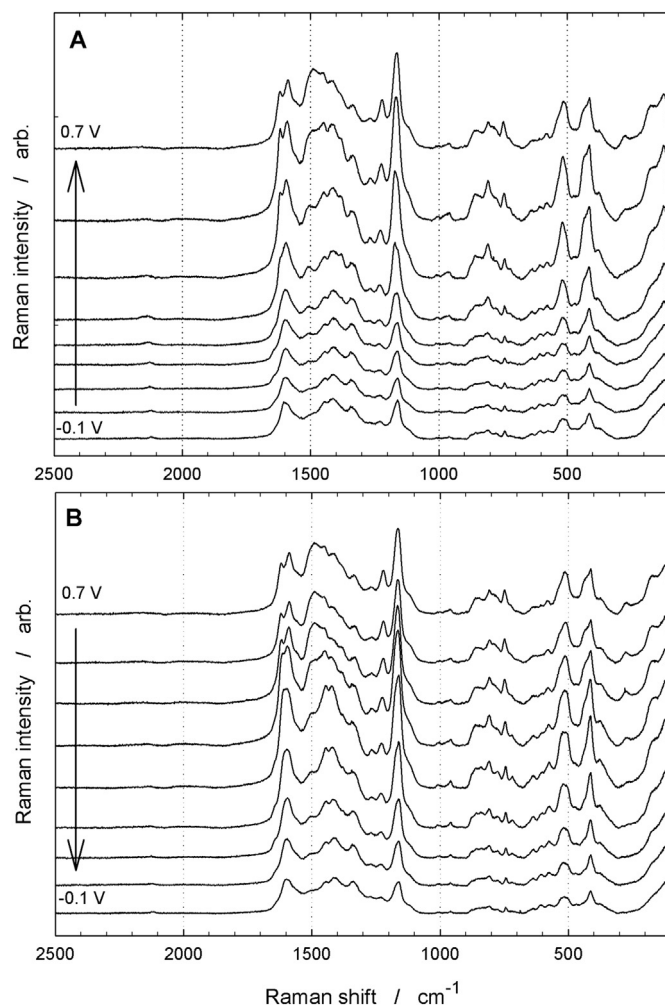


Fig. 1. Raman spectra obtained from a roughened gold electrode modified by the treatment at a controlled potential of  $0.8$  V for  $30$  s in a solution containing  $0.5$  M of sulfuric acid and  $0.05$  M of aniline, and the next following 30-fold potential cycling within the limits of  $0.0$  to  $0.9$  V at a scan rate of  $0.1$  V/s in a solution containing  $0.1$  M of KCl,  $1$  mM of  $K_3Fe(CN)_6$ , and  $1$  mM of  $CuCl_2$ . Spectra were recorded in a solution containing  $0.1$  M of KCl and  $0.1$  M of  $KH_2PO_4$  at electrode potential ranging from  $-0.1$  to  $0.7$  V (A, at the top), or  $0.7$  to  $-0.1$  V (B, at the bottom) at  $0.1$  V intervals (as indicated by arrows).

(PerkinElmer, Inc.) equipped with thermoelectrically cooled up to  $-50$  °C CCD camera and 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  $180^\circ$  scattering geometry was employed. The laser power at the sample was restricted to  $30$  mW and the beam was focused to a  $200$   $\mu$ m 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 thermo-effects, and a possible degradation of PANI or CuHCF layers 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 [19].

## 3. Results and discussion

### 3.1. Spectroelectrochemical properties of composite copper hexacyanoferrate-polyaniline modified electrodes

Two different approaches have been used in the present work for preparation of composite copper hexacyanoferrate and polyaniline modified electrodes. First, polyaniline has been electrodeposited by electropolymerization at a controlled potential from aniline monomer

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