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Electroless Deposition of Metal Hexacyanoferrate on Carbon nanotube Supported Electrode for Electrocatalytic Sensing of Ethanol

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Abstract
The ruthenium oxide-hexacyanoferrate (RuOHCF) was prepared by an electroless deposition method using polymer- Carbon nanotubes (CNTs) composite electrode. The electrochemical and electrocatalytic behavior of RuOHCF modified electrode has been studied. RuOHCF modified electrode exhibits well defined redox peaks for the redox reactions of surface confined redox species. The RuOHCF modified electrode shows excellent electrocatalytic activity towards ethanol and the oxidation of ethanol takes place at 1.1 V, which is much less positive than the unmodified electrode. This electrode is highly stable and sensitive and has been successfully used for the sensing of ethanol at lower concentration.

Keywords*: poly(diallyldimethylammonium) chloride; Carbon nanotubes; Ruthenium oxide-hexacyanoferrate ; Ethanol*

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I. Introduction

The premeditated tailoring of transducers with nanostructured materials is one of the thrilling developments in electroanalytical chemistry. The nanostructured materials have distinctive properties and are very different from their bulk counterpart. Particularly, the nanostructured carbon such as carbon nanotubes (CNTs) has emerged as a new class of materials and received substantial interest since their discovery (1, 2, 3). The CNTs have unique electrical, chemical and mechanical properties. They have been widely used for electroanalytical applications due to their excellent electrocatalytic activity (4). The CNT promoted electrochemical oxidation of hydrogen peroxide, NADH, ascorbate, urate and reduction of oxygen have been well recognized in the literature (4, 5). The CNT tailored transducers have been shown useful to accumulate nucleic acids and avoid surface fouling. The remarkable catalytic effect of CNT permits the utilization of CNT for the development of highly sensitive nanoscale sensor devices and for different catalytic applications. Metal hexacyanoferrates exhibit interesting redox chemistry and are find application in many different areas such as electrocatalysis, electrochromism, electrochemical sensors etc (6-8). Ruthenium has a proven ability to stabilize some polynuclear hexacyanometalates (9-11), and preparation of stable thin films of these electroactive compounds is crucial to their use in an applied capacity.

We have prepared a composite thin film of RuOHCF using CNT based electrode and used for the electrocatalytic sensing of ethanol. Herein we describe electrochemical and electrocatalytic properties of the RuOHCF film prepared by a simple electroless deposition method. In this paper, RuOHCF is prepared by soaking poly(diallyldimethylammonium) chloride (PDA), Multiwall carbon nanotube (CNT) modified composite electrode (PDA-CNT electrode) into aqueous solution of $K_3Fe(CN)_6$ and ruthenium chloride respectively. The resulting RuOHCF-CNT-PDA material brings new capabilities for electrochemical devices by utilizing synergic action of CNT and RuOHCF to facilitate electron-transfer process.

II. Materials and Methods

Reagents and materials

Multi walled CNTs (Cat. No. 636487, ≥ 95% purity), poly(diallyldimethylammonium) chloride (PDA), Ruthenium chloride ($RuCl_3$) and potassium ferricyanide [$K_3Fe(CN)_6$] were purchased from Sigma-Aldrich. All other chemicals used in this investigation were of analytical grade. All solutions were prepared using Milipore water.

Instrumentation

Electrochemical measurements were performed using two-compartment three-electrode cell with a glassy carbon working electrode, a Pt wire auxiliary electrode and Ag/AgCl (3 M NaCl) reference electrode. Cyclic voltammograms were recorded using a computer controlled CHI643B electrochemical analyzer attached to a Picoamp Booster-Faraday cage.

Electroless deposition of RuOHCF on CNT modified electrode

Glassy carbon (GC) electrodes (0.07 cm^2) were used as substrate for making RuOCHF thin film. Before modification with the thin film, the GC electrodes were polished well with fine emery paper and alumina (0.05 μm) slurry and then sonicated in Millipore water for 10-15 min. The polished electrode was thoroughly rinsed with Millipore water and used for modification. A 0.2 mg of purified CNT was dispersed in 100 μL of PDA (1 % solution in water) and stirred in a magnetic stirrer for about 30 min to obtain a homogeneous suspension. An aliquot of 10 μL of the suspension was coated on the GC electrode and allowed to dry at room temperature for 30 min. The RuOHCF modified electrode was been prepared by soaking the PDA/CNTcomposite electrode first in an aqueous solutions of 3mM $K_3Fe(CN)_6$ for 5 min. and then the electrode was subsequently soaked in 3mM $RuCl_3$ for 30 min. Hereafter, the electrode modified with PDA, PDA-CNT and PDA-CNT- RuOHCF will be referred as PDA electrode, PDA/CNT composite electrode and CNT/RuOHCF composite electrode.

This protocol for the electroless deposition of RuOHCF has been optimized based on the current and peak-to-peak separation (ΔE_p) of the redox peaks corresponding to the CNT/RuOHCF composite electrode.

III. Result And Discussion

Fig. 1 shows the cyclic voltammograms obtained for RuOHCF film on CNT-modified electrode. Well-defined redox peaks at -0.06 V, 0.8 V and 1.06 V were observed for the RuOHCF film on the electrode surface in 0.1(M) KNO_3 pH 1.5. The peak current linearly scales with scan rate (data not shown) indicating the redox reaction corresponds to a surface confined redox species. The redox peak is very stable and the peak current and peak potential did not change upon repeated potential cycling, demonstrating that the redox species is very stable and strongly adsorbed on the surface of CNT. Such voltammetric peaks were not observed in the absence of CNT on the electrode surface, suggesting that CNTs play significant role in the generation of the composite film. The electrode prepared in the absence of CNTs (Fig.1B) does not show well-defined voltammogram; only one redox peak corresponding to the redox reaction of surface adsorbed $Fe(CN)_6^{3-/4-}$ couple was observed. The redox peaks I, IV and V for the RuOHCF film can be ascribed to the redox reactions of RuOHCF films (I: [Ru(II)-O/Fe(II)-CN]/ [Ru^{III}-O/Fe^{II}-CN] ; IV: [Ru^{III}-O/Fe^{II}-CN]/ [Ru^{III}-O/Fe^{III}-CN] V: [Ru^{III}-O/Fe^{III}-CN]/ [Ru^{IV}-O/Fe^{III}-CN]) whereas the redox couple III can be attributed to the redox reaction of [Ru^{III}-NC-Fe^{II}]/ [Ru^{III}-NC-Fe^{III}] couple (12).The redox peak II corresponds to the redox reaction of surface adsorbed $Fe(CN)_6^{3-/4-}$ redox couple. This was further confirmed by recording the voltammogram for the couple $Fe(CN)_6^{3-/4-}$ on the CNT modified electrode (data not shown).

Figure 2 illustrates the electrocatalytic effect of the CNT/RuOHCF composite electrode towards ethanol. As can been readily seen, the redox mediator efficiently mediates the oxidation of ethanol according to Scheme 1. Figure 2a corresponds to the CV response of CNT/RuOHCF composite electrode indicating redox couple (IV) and (V). It is clearly seen that only redox couple (V) efficiently mediates the oxidation of ethanol. Enormous increase in the anodic peak associated with a decrease in the cathodic peak has been observed, which demonstrates the strong electrocatalytic effect of the mediator. Note that the onset potential for the oxidation of ethanol is 0.95 V, which is 150 mV negative than the E^0 of redox couple (V), implying the highly efficient nature of the mediator. It is observed that the peak potential shifted to more positive side, when the concentration of ethanol was increased. The sensitivity of the electrode was calculated to be 1.74 μA/mM.

In the absence of RuOCHF, the oxidation of ethanol on the CNT/PDA composite electrode occurred at more positive potential and the voltammogram is not stable. It clearly shows the fact that CNTs plays an important role in decreasing the overpotential for the mediated oxidation of ethanol. The CNTs on the hybrid film facilitates the mediated oxidation of ethanol. The facilitated mediation is attributed to the high electronic and ionic transport capacity of the CNTs on the hybrid film.

IV. Conclusions

Electroless deposition of ruthenium oxide hexacyanoferrate on CNT-based electrode has been used for the electrocatalytic oxidation of ethanol. The CNTs on the composite improved the catalytic efficiency of the mediator. This electrode is stable and can detect ethanol in the micro molar level. Though the present transducer could detect the ethanol at higher potential (1.1 V), this can be used for the non enzymatic sensing of ethanol in real sample analysis. Further works are in progress.

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Figures

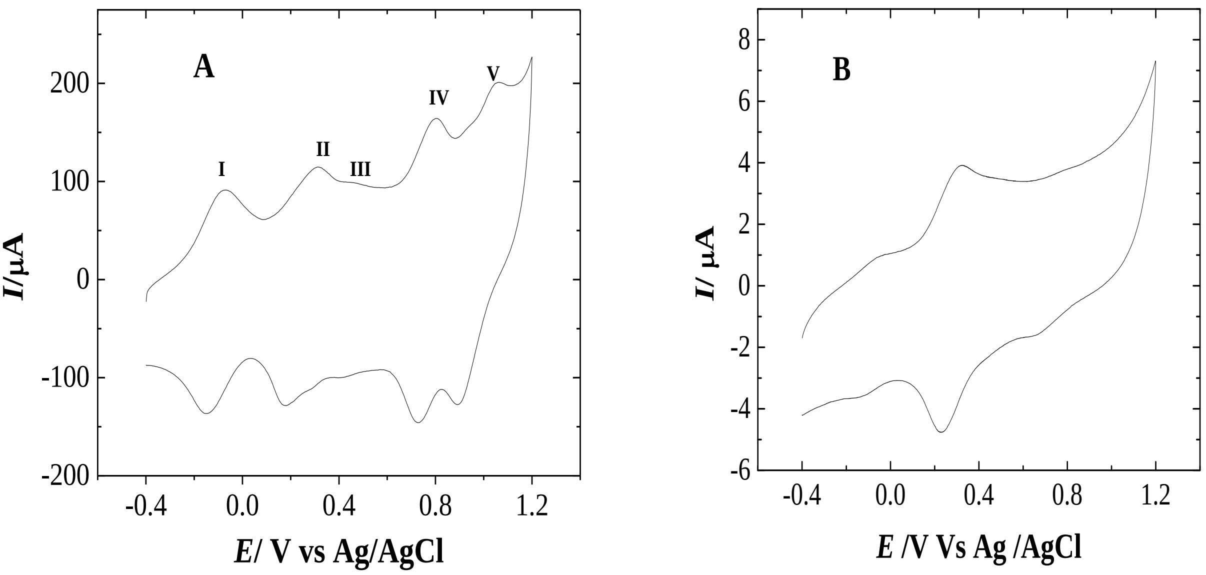


Figure 1 (A) Cyclic voltammogram of the CNT/RuOHCF composite electrode in KNO_3 pH 1.5 at 100mV/s. (B) Cyclic voltammogram of the RuOHCF composite electrode in KNO_3 pH 1.5 at 100mV/s.

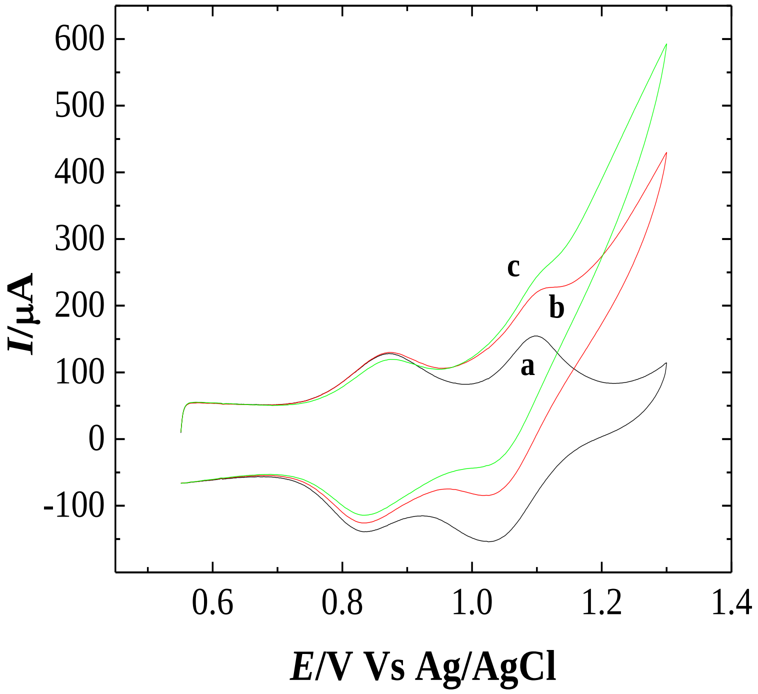
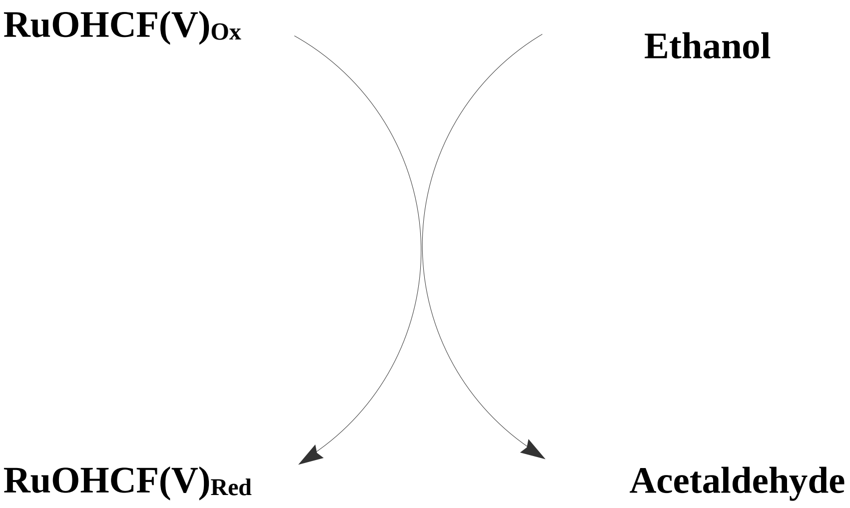


Figure 2 Electrocatalytic activity of CNT/RuOHCF composite electrode towards ethanol in KNO_3 (pH 1.5). [Etanol]: (a) 0, (b) 35mM and (c) 70mM. Scan rate: 50mV/s.



Scheme 1 Schematic illustration for the mediated oxidation of ethanol on CNT/RuOHCF composite electrode.