



Characterization of Ruthenium Based Metal Complex Nanoparticles Decorated on Carbon Supported Surface

Sudip Chakraborty^{1*} and Nabakumar Pramanik²

¹Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, INDIA

²Department of Chemistry, National Institute of Technology, Arunachal Pradesh, INDIA

Available online at: www.isca.in

Received 17th November 2012, revised 25th November 2012, accepted 7th January 2013

Abstract

The ruthenium oxide-hexacyanoferrate nanoparticles (RuOHCNP) were prepared by an electroless deposition approach and the electrochemical, spectral and morphological behavior of RuOHCNP modified electrode has been investigated. RuOHCNP were well decorated on the walls of carbon nanotubes and shows stable voltammetric response. This electrode is highly stable with high reproducibility.

Keywords: Carbon nanotubes, ruthenium oxide-hexacyanoferrate nanoparticles, voltammetry.

Introduction

The deliberate tuning of electrochemical interface with nano-materials is one of the exciting developments in the field of electroanalytical sensor and biosensor. The nanostructured carbon such as carbon nanotubes (CNTs) has emerged as a new class of materials and received considerable interest since their discovery^{1,2} as they have unique electrical, chemical and mechanical properties. They have been widely used for the fabrication of electroanalytical sensors and bio-sensors due to their excellent electrocatalytic activity³. The CNT assisted electrochemical oxidation of hydrogen peroxide; NADH, ascorbate and reduction of oxygen have been well documented⁴. The CNT tailored electrochemical interfaces have been shown useful to avoid surface fouling. The outstanding catalytic effect of CNT permits the utilization of CNT for the development of highly sensitive nanoscale sensor devices and for different catalytic applications. Hexacyanoferrates of different transition metals display attractive redox chemistry and are find application in many different areas such as electrocatalysis, electrochromism, electrochemical sensors etc.⁵ Among the metal hexacyanoferrates, ruthenium oxide hexacyanoferrate (RuOHCNP) was studied for its interesting chemical and electrochemical properties. Ruthenium has ability to stabilize some polynuclear hexacyanometalates^{6,7}, and preparation of stable thin films of these electroactive compounds is critical to their use in a functional capacity.

We have prepared a composite thin film of RuOHCNP using CNT based electrode according to the procedure mentioned in the literature⁸ and used for the amperometric sensing of ethanol. Researchers have synthesized the modified film electrodes using repetitive cyclic voltammetry to form polynuclear mixed-valent ruthenium oxide/ ruthenocyanide films on various electrodes directly from solutions containing Ru⁺³ and Fe(CN)₆³⁻ ions and various electrolyte⁹. Films have also been directly synthesized

using repetitive cyclic voltammetry from Ru³⁺ and Fe(CN)₆³⁻¹⁰. Herein we describe the spectral, morphological and electrochemical of the RuOHCNP.

Material and Methods

Multi walled CNTs ($\geq 95\%$ purity), Poly-diallyl dimethyl ammonium chloride (PDA), Ruthenium chloride (RuCl₃) and potassium ferricyanide [K₃Fe(CN)₆] were purchased from Sigma-Aldrich. All other chemicals used in this investigation were of analytical grade. All solutions were prepared using Millipore 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. JEOL JEM 6700F field emission scanning electron microscope (FESEM) was used to obtain FESEM images of the PDDA dispersed CNT and RuOHCNP deposited CNT.

Electroless deposition of RuOHCNP on CNT modified electrode: We have prepared a composite thin film of RuOHCNP using CNT based electrode according to the following procedure mentioned in the literature⁸. GC electrodes (0.07 cm²) were used as substrate for making RuOHCNP thin film. Before modification with the thin film, the GC electrodes were polished well with fine emery paper and alumina (0.05 μ m) 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 μ L 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 RuOHCFNP modified electrode was prepared by soaking the PDA/CNT composite electrode first in an aqueous solution of 3mM $\text{K}_3\text{Fe}(\text{CN})_6$ 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- RuOHCFNP will be referred as PDA electrode, PDA/CNT composite electrode and CNT/RuOHCFNP composite electrode.

Results and Discussion

Figure 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 redox peaks I, IV and V for the RuOHCFNP film can be ascribed to the redox reactions of RuOHCFNP films (I: $[\text{Ru}(\text{II})\text{-O}/\text{Fe}(\text{II})\text{-CN}]/[\text{Ru}^{\text{III}}\text{-O}/\text{Fe}^{\text{II}}\text{-CN}]$; IV: $[\text{Ru}^{\text{III}}\text{-O}/\text{Fe}^{\text{II}}\text{-CN}]/[\text{Ru}^{\text{III}}\text{-O}/\text{Fe}^{\text{III}}\text{-CN}]$ V: $[\text{Ru}^{\text{III}}\text{-O}/\text{Fe}^{\text{III}}\text{-CN}]/[\text{Ru}^{\text{IV}}\text{-O}/\text{Fe}^{\text{III}}\text{-CN}]$) whereas the redox couple III can be attributed to the redox reaction of $[\text{Ru}^{\text{III}}\text{-NC-Fe}^{\text{II}}]/[\text{Ru}^{\text{III}}\text{-NC-Fe}^{\text{III}}]$ couple¹¹. The redox peak II corresponds to the redox reaction of surface adsorbed $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. This was further confirmed by recording the voltammogram for the couple $\text{Fe}(\text{CN})_6^{3-/4-}$ on the CNT modified electrode (figure 2). Figure 2 displays the CV response of the adsorbed $\text{Fe}(\text{CN})_6^{3-/4-}$ onto the PDA/CNT composite electrode and PDA-electrode (figure 2 inset). It is interesting to note that

in the presence of CNT current corresponding to the redox species is too high compared to the composite in absence of CNT. The adsorption of the redox species have been made by simple soaking the electrode into the 3 mM aqueous solution of $\text{K}_3\text{Fe}(\text{CN})_6$ for 30 mins. As the polymer PDA is positively charged at the present experimental condition, the negatively charged $\text{Fe}(\text{CN})_6^{3-/4-}$ adsorbed on the electrode surface by the electrostatic interaction. The formation of the RuOHCFNP film is highly favorable due to the presence of CNT-PDA composite on the electrode surface. The FESEM image in Figure 3B confirmed the formation of RuOHCF nanoparticles displaying the diameter of the particle is ~ 70 nm. Figure 3A displays the typical FESEM image of the CNT with diameter between ~ 30 and 80 nm. It is notable that presence of PDA makes the well association of CNTs. According to the previous literature, shape of metal hexacyanoferrates are different because of their different synthetic procedure^{12,13}, but we are reporting first time about the deposition of RuOHCF nanoparticles by a simple electroless method. Figure 4 displays the spectral behaviour of RuOHCF nanoparticles. UV-Visible absorption spectra for PDA-CNT- $\text{Fe}(\text{CN})_6^{3-}$ composite coming ~ 420 nm whereas CNT/RuOHCFNP composite exhibits three peaks at 420, 480 and 595 nm respectively (figure 4a). This UV-visible absorption peak patterns are similar to the absorption spectra of RuOHCF (5). But the RuOHCFNP composite without CNT exhibits no well defined characteristic absorption peak (figure 4b), which indicates that presence of CNTs are critically essential for the electroless deposition of RuOHCFNP.

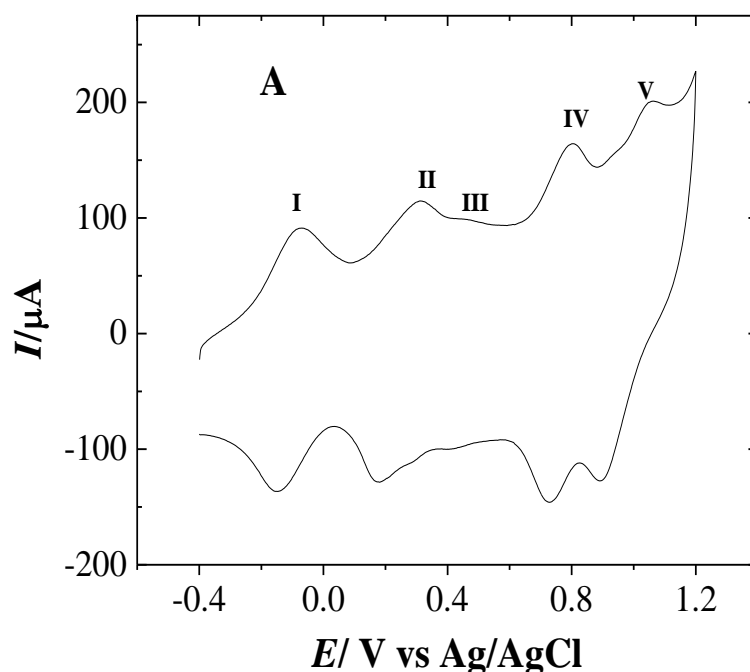


Figure-1
Cyclic voltammogram of the CNT/RuOHCF composite electrode in KNO_3 pH 1.5 at 100mV/s

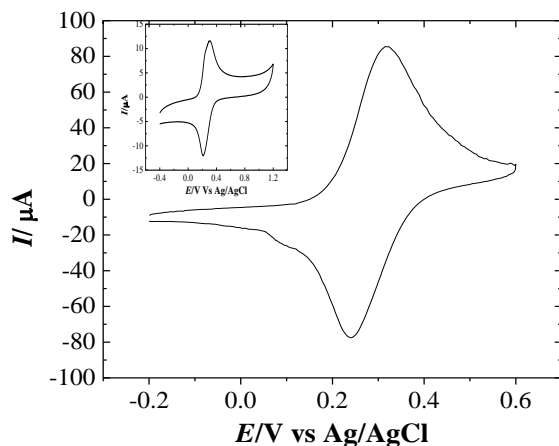


Figure-2

Cyclic voltammogram of the PDA/CNT/Fe(CN)₆^{3-/4-} electrode in 0.1M KNO₃ pH 1.5 at 100 mV/s. Inset shows Cyclic voltammogram of the PDA /Fe(CN)₆^{3-/4-} electrode in 0.1M KNO₃ pH 1.5 at 100 mV/s

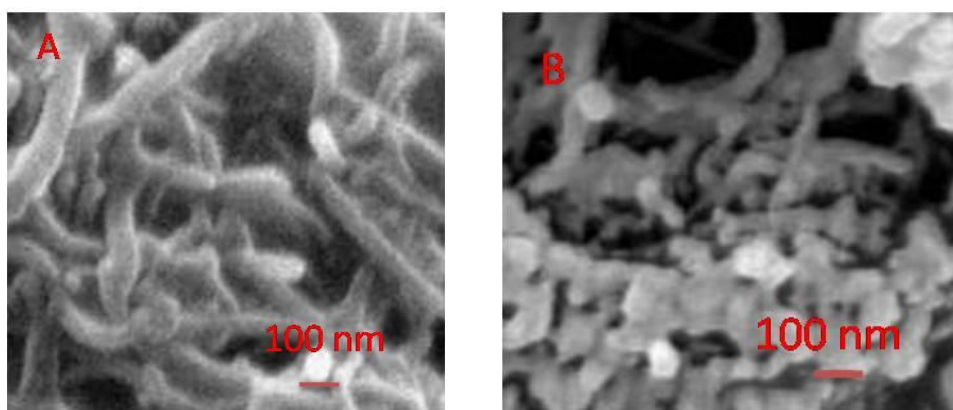


Figure-3

(A) FESEM image of PDA/CNT composite and (B) FESEM image of CNT/RuOHCfNP composite.

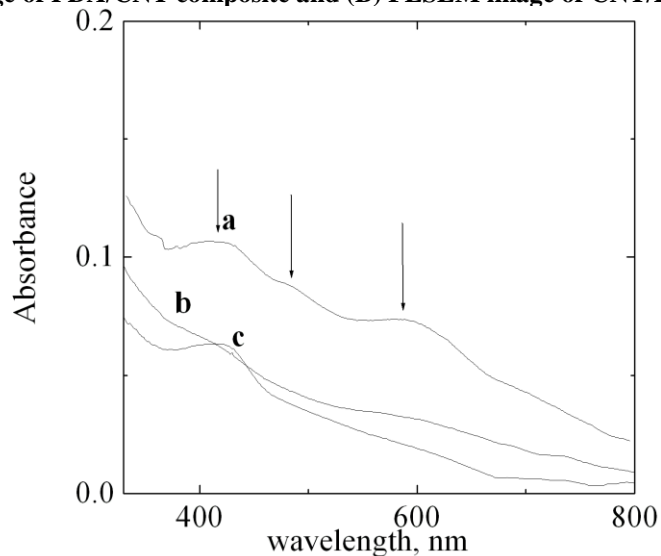


Figure 4

UV-visible absorption spectra of (a) CNT/RuOHCfNP composite (b) RuOHCfNP composite and (c) CNT/ Fe(CN)₆³⁻ composite

Conclusion

Electroless deposition of ruthenium oxide hexacyanoferrate nanoparticles on CNT-based electrode has been characterized. The electrochemical, spectral, and morphological behavior of RuOHCFNP modified electrode has been investigated. As the protocol for the preparation of electrode is very simple, it can be easily prepared daily. RuOHCFNP modified electrode can be used to bring new capabilities for electrochemical devices by utilizing synergic action of CNT and RuOHCFNP to facilitate electron-transfer process.

Acknowledgements

SC thanks IIT-Kharagpur, India and NP thanks NIT-Arunachal Pradesh for support.

References

1. Iijima S., Helical microtubules of graphitic carbon, *Nature*, **354**, 56 (1991)
2. Wong E.W., Sheehan P.E. and Lieber C.M., Nanobeam Mechanics: Elasticity, Strength and Toughness of Nanorods and Nanotubes, *Science*, **277**, 1971 (1997)
3. Wang J., Carbon-Nanotube Based Electrochemical Biosensors: A Review, *Electroanalysis*, **17**, 7 (2005)
4. Gong K., Dong Y., Xiong S., Chen Y. and Mao L., Novel electrochemical method for sensitive determination of homocysteine with carbon nanotube-based electrodes, *Biosens. Bioelectron.*, **20**, 253 (2004)
5. Cox J.A. and Kulesza P.J., Electrochemical oxidation and determination of arsenic(III) on a glassy carbon electrode modified with a thin film of mixed-valent ruthenium(III, II) cyanide, *Anal. Chem.*, **56**, 1021 (1984)
6. Itaya K., Ataka T. and Toshima S., Spectroelectrochemistry and electrochemical preparation method of Prussian blue modified electrodes, *J. Am. Chem. Soc.*, **104**, 4767 (1982)
7. Zhou D.M., Ju H.X. and Chen H.Y., Catalytic oxidation of dopamine at a microdisk platinum electrode modified by electrodeposition of nickel hexacyanoferrate and Nafion, *J. Electroanal. Chem.*, **408**, 219 (1996)
8. Chakraborty S. and Pramanik N., Electroless Deposition of Metal Hexacyanoferrate on Carbon nanotube Supported Electrode for Electrocatalytic Sensing of Ethanol, *Int. J. Eng. Res. Application.*, **2**, 1015 (2012)
9. Chen S.M. and Hsueh S.H., Preparation, characterization and electrocatalytic properties of polynuclear mixed-valent ruthenium oxide/hexacyanoruthenate film modified electrodes, *J. Electroanal. Chem.*, **566**, 291 (2004)
10. K. Kasem, F.R. Steldt, T.J. Miller, A.N. Zimmerman, Electrochemical synthesis of zeolite-like ruthenium-based hexacyanometalates multi-film assemblies, *Microp. Mesop. Mater.*, **66**, 133 (2003)
11. Chen S.M., Lu M. and Lin K., Preparation and characterization of ruthenium oxide/hexacyanoferrate and ruthenium hexacyanoferrate mixed films and their electrocatalytic properties, *J. Electroanal. Chem.*, **579**, 163 (2005)
12. N. R. de Tacconi and K. Rajeshwar, Metal Hexacyanoferrates: Electrosynthesis, in Situ Characterization, and Applications, *Chem. Mater.*, **15**, 3046 (2003)
13. Yang M., Jiang J., Yang Y., Chen X., Shen G. and Yu R., Carbon nanotube/cobalt hexacyanoferrate nanoparticle-biopolymer system for the fabrication of biosensors, *Biosens. Bioelectron.*, **21**, 1791 (2006)