



Electrocatalytic behaviour of hybrid cobalt–manganese hexacyanoferrate film on glassy carbon electrode



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ABSTRACT

A thin film of hybrid cobalt–manganese hexacyanoferrate (CoMnHCF), a redox mediator was electrodeposited on a glassy carbon (GC) electrode and was employed as an amperometric sensor towards L-Tryptophan (L-Trp). The hybrid film was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction technique (XRD), scanning electron microscope–energy dispersive X-ray spectroscopy (SEM–EDAX), and electrochemical techniques. The atomic absorption spectroscopic analysis provided the stoichiometry of the hybrid film to be $K_{1.74-y}Co_yMn_{0.78}[Fe(CN)_6]_y$, $y \leq 0.68$. The electrochemical impedance study revealed the excellent charge transfer properties of GC/CoMnHCF electrode. The voltammetric investigations demonstrated exceptional electrocatalytic properties of the hybrid film modified electrode when compared to that of bare GC, GC/CoHCF and GC/MnHCF electrodes, towards the L-Trp oxidation. The kinetic parameters such as electron transfer coefficient, the electron transfer rate constant, the diffusion coefficient and the catalytic rate constant for the electrooxidation process of L-Trp were investigated. The amperometric detection of L-Trp employing GC/CoMnHCF electrode possessed a good sensitivity of $10 \times 10^{-2} A M^{-1} cm^{-2}$ in a wide range of detection (2–200 μM) at a reduced overpotential of 680 mV. In addition, the proposed amperometric method was applied to the detection of L-Trp in commercial milk samples with reproducible results.

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1. Introduction

Electrochemical sensors have been widely used due to its salient features such as fast response time, sensitivity, accuracy, excellent selectivity and repeatability. Carbon is one of the inexpensive substrate used for electrochemical techniques (such as glassy carbon, carbon paste, carbon fibre, carbon nanotubes), but its over potential makes the selective detection of environmental compounds impossible, especially for biomolecules. So chemically modified carbon based electrodes [1] have been centred much attention in this field, as they increase the electron transfer kinetics between the electrode–electrolyte interface. In this scenario, redox mediators like metal hexacyanoferrates (MHCFs) have been attracting electrochemists because of its excellent electron transfer properties, electrocatalytic and electrochromic activities [2–4], charge compensation properties [5], and its capability to detect organic and inorganic species [6]. In recent years, several MHCFs have been reported; ZnHCF [7], MnHCF [8], CoHCF [9], PdHCF [10], PtHCF [11], AgHCF [12], CuHCF [13], NiHCF [14] SnHCF [15], and hybrid MHCFs such as NiPdHCF [16], NiCoHCF [17], and NiTiHCF [18] are the few

examples. Direct modification of the electrode surface provides higher stability for the hexacyanoferrate film, which avoids the accumulation of substances on to the electrode, further enhancing the electrode response towards the biomolecules. The hybrid CuCoHCF modified carbon paste electrode as a L-Cysteine sensor [19], nafion–cobalt hexacyanoferrate film modified electrode [20] for dopamine detection, hybrid CuCoHCF modified graphite electrode [21] as a L-Tryptophan (L-Trp) sensor and a Prussian blue–graphene oxide based glucose biosensor, [22] etc., are some of the MHCF based electrochemical sensors designed in the past few years that have given promising results.

Detection of amino acids possesses significant importance in various fields of research particularly in microbiology, food science, agricultural environmental engineering, and pharmaceutical industries. L-Trp is an essential amino acid for humans and herbivores and also acts as a precursor to serotonin, a neurotransmitter, and melatonin, a neurohormone. It is a common ingredient of many proteins and has a vital role in controlling the biochemical balance of the brain and is essential for people having sleep deprivation, anxiety and mood enhancement, because of its ability to increase serotonin and melatonin presence in brain cells. L-Trp also helps in maintaining the positive balance of nitrogen. Hence L-Trp is an essential part of human diet and this makes it important in pharmaceutical preparations and food products. The improper metabolism of L-Trp generates a toxic side product in the brain which can cause hallucination, delusions and schizophrenia [23]. The excess L-Trp in our body can cause imbalance of nitrogen gas

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in adults, confusion, fever, agitation, nausea, diarrhoea, etc. Therefore, a simple, cheap and sensitive analytical detection technique is required to measure the concentration of L-Trp. Several analytical procedures have been developed for the detection of L-Trp, such as fluorometry [24], chemiluminescence [25], capillary electrophoresis [26], spectrometry [27], and high-performance liquid chromatography, [28]. But these are expensive, time consuming techniques and require excess amount of solvents. The electroanalytical techniques that overcome these problems are more appropriate for the quantification of L-Trp.

The redox and electrocatalytic properties of hybrid cobalt manganese hexacyanoferrate (CoMnHCF) film were not yet reported. Hence the present study focussed on the electrodeposition of CoMnHCF as a thin film on glassy carbon (GC) electrode. The modified electrode exhibited appreciable electrocatalytic properties towards the oxidation of L-Trp. Also, the proposed sensor was applied for the detection of L-Trp in commercial milk samples to illustrate its reliability.

2. Experimental details

2.1. Reagents and solutions

L-Trp, L-Tyrosine, L-Cysteine, Urea, Uric acid, LiCl and CsCl were purchased from Alfa Aesar. KH_2PO_4 , K_2HPO_4 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, O, KCl, KNO_3 and NaCl were purchased from Merck and were used as obtained. All reagents used in this work were of analytical reagent grade and all solutions were prepared in ultrapure water from Millipore-Q unit (Milli-Q water purifiers use resin filters and deionization technique to purify the water; resistivity: 18.2 M Ω .cm at 25 °C). L-Trp stock solution was prepared in 0.1 M phosphate buffer solution (PBS) of pH 7.

2.2. Apparatus and electrodes

CoMnHCF film electrodeposited over indium tin oxide (ITO) coated glass slide (1 cm²) was used for Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and scanning electron microscope–energy dispersive X-ray (SEM–EDAX) analyses and the same electrodeposited over a stainless steel plate (surface area: 7 cm²) was used for atomic absorption spectroscopic (AAS) studies. Thermo scientific Nicolet iS5 FT-IR spectrometer was used for recording the FT-IR spectra. The XRD study was conducted by using Philips XRD with $\text{K}\alpha$ of Cu (0.154 nm) as the source and SEM–EDAX with Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM). A GBC make double beam Atomic Absorption Spectrophotometer, Australia, was employed for the elemental analysis of the hybrid hexacyanoferrate film. Electrochemical analyzer (CHI6043B, CH instruments, USA) coupled with a three electrode cell was used for electrochemical studies. A GC electrode of 3 mm diameter, a Pt wire and a saturated Ag/AgCl electrode was used as the working electrode, counter electrode and reference electrode respectively. Electrochemical impedance measurements were performed with the bare and modified electrodes as working electrodes at open circuit potential in the frequency range of 10 mHz to 100 kHz in 0.1 M PBS of pH 7.

2.3. Procedure

The GC electrode was polished with alumina slurries having different particle size of 1, 0.3 and 0.05 μm , washed with ultra pure water and further 5 min sonication prior to use. This electrode was further washed with ethanol and then with water. The hybrid CoMnHCF was electrodeposited by applying continuous cycles in the range of -0.2 to 1 V from a solution mixture containing 0.5 mM CoCl_2 , 0.5 mM MnCl_2 , 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl (20 cycles). Freshly prepared solutions were used in all stages in order to obtain reproducible results

and should be added in the following order under stirring condition: KCl, CoCl_2 , MnCl_2 , and $\text{K}_3\text{Fe}(\text{CN})_6$. After electrodeposition, the modified electrode was washed thoroughly with distilled water and was kept in KCl solution.

In order to compare the electrocatalytic activity of the hybrid hexacyanoferrate film modified electrode with the individual hexacyanoferrate film modified electrodes such as GC/CoHCF and GC/MnHCF electrodes, the films were electrodeposited from the corresponding metal ion solutions by following the previously mentioned procedure. CoMnHCF modified ITO coated glass slides were prepared by applying 75 continuous cycles in order to carry out FT-IR, XRD and EDAX analyses.

The stoichiometry of CoMnHCF film was determined by AAS analysis. Co, Mn, Fe and K were quantified from the sample solution at its characteristic wavelength of 240.7, 279.5, 248.3 and 766.5 nm respectively. The CoMnHCF film was electrodeposited by applying 75 continuous cycles onto a stainless steel plate and the sample solutions were prepared by dissolving the film in 2.0 cm³ hot concentrated hydrochloric acid. The process was repeated five times, each time using the same hydrochloric acid followed by dilution to 10 cm³ before all atomic absorption measurements. The blank solution and the standard solutions were also prepared by using the same level of hydrochloric acid.

3. Results and discussion

3.1. Structure of hybrid CoMnHCF film

The anodic and cathodic peak currents were found to increase linearly with the electrodeposition process up to 20 cycles and further no change was observed (Fig. 1A). The hybrid CoMnHCF film was characterized by FT-IR, XRD, and SEM–EDAX analyses. The prominent peak

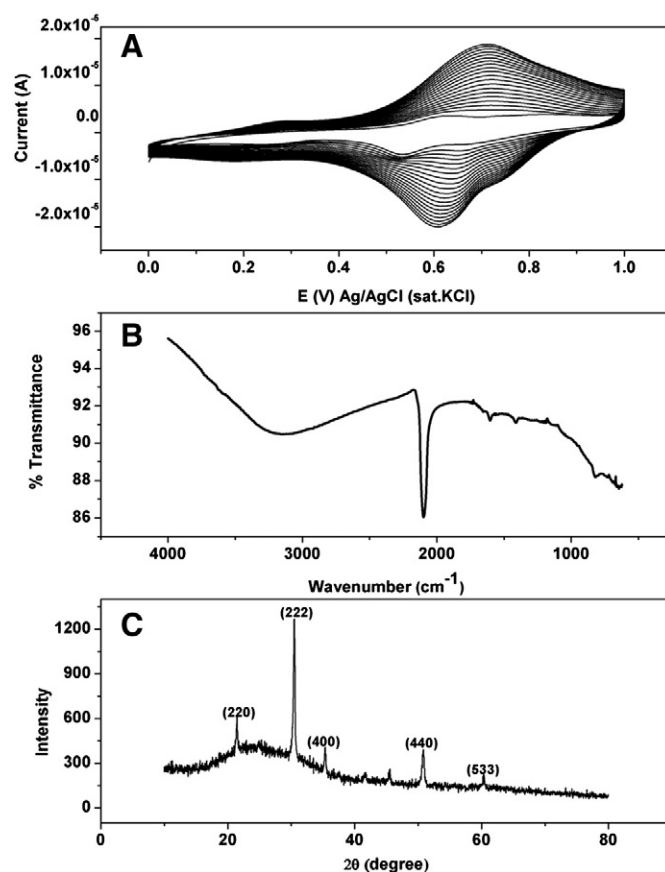


Fig. 1. (A) Voltammograms of electrodeposition of CoMnHCF on GC electrode, (B) FT-IR spectrum and (C) XRD pattern of CoMnHCF film on ITO surface.

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