Electrochimica Acta 105 (2013) 439–446

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical synthesis of dysprosium hexacyanoferrate micro stars incorporated multi walled carbon nanotubes and its electrocatalytic applications

Muniyandi Rajkumar, Balamurugan Devadas, Shen-Ming Chen*

Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC

A R T I C L E   I N F O

Article history:
Received 20 December 2012
Received in revised form 21 April 2013
Accepted 30 April 2013
Available online 13 May 2013

Keywords:
Electrochemical synthesis
Dysprosium hexacaynoferrate
Micro stars
Dopamine
Uric acid
Selective determination

A B S T R A C T

Herein, we report template free, surfactant less, fabrication of dysprosium hexacyanoferrate (DyHCF) micro stars by simple electrochemical deposition process. The electrochemical measurements and surface morphology of the as prepared composite electrode are studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FESEM). The synthesized DyHCF micro stars are characterized by Fourier transmitted infra-red spectroscopy (FTIR), X-ray diffraction (XRD) and ultra violet spectroscopy, respectively. The size of the micro stars are controlled by, controlling the number of electrodepositing cycles. The amount of multi walled carbon nanotubes (*f*MWCNTs) loading are optimized by EIS analysis. The presence of the *f*MWCNTs in the film enhances the surface coverage concentration and also increases the electron transfer rate constant, of the DyHCF micro stars. This DyHCF incorporated multi walled carbon tube modified electrode (DyHCF/*f*MWCNTs) exhibits a prominent electrocatalytic activity toward the selective detection of DA and UA in presence of AA. The peaks of the AA, UA, and DA get separated well in the DyHCF–*f*MWCNTs modified electrode with potential value of 250 mV (between AA and DA) and 320 mV (between AA and UA). The modified electrode shows the linear range of 3–137 μM for UA and DA. The proposed film also successfully used for the selective detection of DA and UA in the presence of AA in human urine samples with a linear range of 3–289 μM. Well separated peak for the detection of UA and DA in urine has proven this DyHCF/*f*MWCNTs modified electrode as a successful biosensor.

1. Introduction

In recent years, synthesis and investigation of the electrochemical behavior of metal hexacyanoferrate (MHCF) have attracted considerable attention due to their ability to mediate number of electrocatalytic processes. In particular, high stability of the metal cyanide framework in MHCFs and the possibility for cation exchange between a solution and the cages of framework has made these metal complexes based research much more interesting [1]. To date, many researchers have investigated several MHCFs and their potential application in the field of electrochemistry [2,3]. In the course of the developments MHCF have been made as nanoparticles and electrochemically characterized by several researchers [4]. Owing to the large surface area, good conductivity and outstanding catalytic activity, MHCF nanoparticles have been widely used for the development of electrochemical sensors [5,6] and biosensors applications [7,8]. In the series of different MHCF developments, rare earth metal dysprosium hexacyanoferrate (DyHCF) also prepared and applied for the catalytic purposes [9–12]. These preparation methods are chemical and do not show any specific structure to the DyHCF.

On the other hand, there is a constant requirement to develop a sensor for the biologically important compounds dopamine (DA), uric acid (UA) and ascorbic acid (AA) which usually coexist together and considered as important molecules for physiological processes in human metabolism. UA and DA deficiencies result in several diseases and disorders [13–16]. The first species plays an important role in human brain and a loss of DA-containing neurons may result in some serious diseases such as Parkinson. The main difficulty with the electrochemical detection of DA in brain fluids is the coexistence of many interfering compounds. Among these, ascorbic acid (AA) and UA are of particular importance; these compounds may be present in relatively high concentration (100–500 mM for AA and 1–50 mM for UA), while baseline dopamine level is of the order of 50 nM [17]. In clinical point of view, detection of UA in urine also shares a similar importance and this again has interference from AA. Thus, researchers are keen on developing biosensor for the selective detection of dopamine (DA) and uric acid (UA). But,

---

* Corresponding author. Tel.: +886 2270 17147; fax: +886 2270 25238.
E-mail address: smchen78@ms15.hinet.net (S.-M. Chen).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.04.172

determination of DA and UA on solid electrodes is challenging one due to the overlapping oxidation peak potentials.

There are few film modified electrodes have been reported for the selective determination of these compounds in the presence of ascorbic acid such as 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane modified glassy carbon electrode [18], graphite oxide bulk modified carbon paste electrode [19], polymerized luminol film modified glassy carbon electrode [20], and bio sensing properties of titanate-nanotube films [21] new polymeric composite film [22]. These electrochemical sensors satisfied many of the requirements such as specificity, speed of response, sensitivity and simplicity of preparation. However, the utilities of solid-electrode-based sensors are often hampered by not having sufficient selectivity. In particular, complexity of real biological systems may result in overlapping voltammetric signals.

Here we report a simple electrochemical method to prepare DyHCF and achieved specific micro star structure. This redox complex with the micro star structure was employed for the selective electrocatalytic determination of UA and DA by making DyHCF–*f*MWCNTs composite. This composite was prepared on GCE and ITO electrodes by simple two steps process electrodeposition of DyHCF followed by drop casting of *f*MWCNTs. As prepared electrode was characterized using surface analysis technique FESEM along with electrochemical techniques CV and EIS. DyHCF/*f*MWCNTs modified electrode successfully separated UA and DA without AA interference and quantified in real system in urine sample using differential pulse voltammetric (DPV) method.

2. Experimental

2.1. Apparatus

Electrochemical measurements like cyclic voltammogram (CV) and differential pulse voltammogram were performed by using a CHI 1205 A electrochemical analyzer. A conventional three-electrode cell was used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by FESEM (Hitachi, Japan). Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik GmbH & Co. KG, Germany).

2.2. Materials

Dysprosium(III) chloride hexahydrate, multi walled carbon nanotubes, ascorbic acid (AA), dopamine (DA) and uric acid (UA) were purchased from Sigma–Aldrich. Potassium hexacyanoferrate(III) was purchased from Wako Pure Chemical Industries and AA, DA and UA solutions were freshly prepared every day. The other chemicals (Merck) were used in this investigation with analytical grade (99%). All the solutions were prepared using doubly distilled water. Electrocatalytic studies were carried out in 0.2 M KCl solution. Pure nitrogen gas was purged through all the experimental solutions for removing dissolved oxygen.

2.3. Preparation of fMWCNTs and electrochemical fabrication of DyHCF/fMWCNTs composite modified electrode

There was an important challenge in the preparation of *f*MWCNTs. Because of its hydrophobic nature, it was difficult to disperse it in any aqueous solution to get a homogenous mixture. Briefly, the hydrophobic nature of the MWCNTs was converted in to hydrophilic nature by following the previous studies [23,24]. The pretreatment and functionalization of MWCNTs was done by suspending 150 mg of MWCNTs in mixture of concentrated sulfuric acid–nitric acid (3:1, v/v) and sonicated for 2 h. After that a nanotube mat was obtained and was filtered using a 0.45 mm hydrophilized PTFE membrane and washed with deionized water until the pH becomes 7 and kept for drying under vacuum. 10 mg of thus obtained *fMWCNTs* was dissolved in 10 ml water and ultrasonicated for 6 h to get a uniform dispersion. This process not only converts *f*MWCNTs to hydrophilic nature but this helps to breakdown larger bundles of the *f*MWCNTs into smaller ones.

Prior to the electrodeposition process, the bare glassy carbon electrode was initially polished with 0.05 μM alumina powder using BAS polishing kit and ultrasonically cleaned in water for a minute. The electrode was then washed with double distilled water and utilized for further electrodeposition. The DyHCF particles are electrochemically deposited on the GCE from 0.2 M KCl solution containing 1×10^{-2} M $DyCl_3 \cdot 6H_2O$ and 1×10^{-2} M $K_3\,Fe(CN)_6$, with a repetitive potential scan between 0.8 and −0.2 V (at the scan rate of 100 mV/s) for twenty cycles [25]. Then 5 μl of as prepared *f*MWCNTs was drop casted on the DyHCF modified electrode to form DyHCF/*f*MWCNTs composite film. Then the DyHCF/*f*MWCNTs modified GCE was rinsed with deionized water and applied for the further electrochemical studies.

3. Results and discussion

3.1. Electrochemical characterization of DyHCF/fMWCNTs modified electrode

Fig. 1A shows the cyclic voltammogram (CV) of DyHCF micro stars deposition process. Here the CV shows the characteristic current features of a cathodic peak corresponding to the reduction of $Fe(CN)_6{}^{3-}$ to $Fe(CN)_6{}^{4-}$ appears at 0.223 V and the anodic peak corresponding to the oxidation of $Fe(CN)_6{}^{4-}$ to $Fe(CN)_6{}^{3-}$ appears at 0.313 V. On scanning the potential back to 0.8 V, it clearly shows the peaks currents corresponds to the reaction of $Fe(CN)_6{}^{3-/4-}$ redox couple decrease gradually with the increase of the scan cycles, which validates the formation of DyHCF film on the electrode surface. The Dy^{3+} ions reacted with $Fe(CN)_6{}^{4-}$ to form DyHCF film on the electrode surface. Here the equivalent molar concentrations (10^{-2} M) of dysprosium and hexacyanoferrate have been taken for the balanced deposition of DyHCF film. These observations clearly suggest that the successive formation of DyHCF film on the GCE surface. Furthermore 5 μl of *f*MWCNTs was drop casted on DyHCF modified GCE. The formation of DyHCF on the electrode surface can be expressed by the following reaction mechanism.

$$Fe(CN)_6{}^{3-} + e^- \rightarrow Fe(CN)_6{}^{4-} \quad (1)$$

$$Fe(CN)_6{}^{4-} + Dy^{3+} + K^+ \rightarrow KDyFe(CN)_6 \quad (2)$$

In the next step, the prepared DyHCF/*f*MWCNTs electrode was transferred into pH 7 PBS for scan rate studies. Fig. 1B shows the cyclic voltammograms obtained at DyHCF/*f*MWCNTs composite electrode in N_2 saturated PBS solution (pH 7) at different scan rate studies. Both Ipa and Ipc increased linearly with increase in scan rates between 0.01 and 0.1 V/s. This indicated that the electron transfer process occurring at DyHCF/*f*MWCNTs composite film is a surface confined process. The peak currents (Ipa and Ipc) vs. scan rates plot is shown in Fig. 1B, inset. Both Ipa and Ipc exhibited linear relationship with scan rates, R^2 = 0.991 and 0.999, respectively.