



Improved L-cysteine electrocatalysis through a sequential drop dry technique using multi-walled carbon nanotubes and cobalt tetraaminophthalocyanine conjugates



Stephen Nyoni^a, Tawanda Mugadza^{a,b}, Tebello Nyokong^{a,*}

^a Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

^b Department of Chemical Technology, Midlands State University, P. Bag 9055, Gweru, Zimbabwe

ARTICLE INFO

Article history:

Received 8 June 2013

Received in revised form

24 September 2013

Accepted 1 October 2013

Available online 19 October 2013

Keywords:

L-Cysteine

Cyclic voltammetry

Chronoamperometry

Scanning electrochemical microscopy

Impedance spectroscopy

Cobalt tetraaminophthalocyanine

ABSTRACT

Voltammetry, chronoamperometry, scanning electrochemical microscopy and electrochemical impedance spectroscopy methods are used for characterization of a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNTs)–cobalt tetraaminophthalocyanine (CoTAPc) mixture or sequential drop dry modification technique whereby the MWCNTs are first placed on to the electrode followed by CoTAPc. The sequential drop dry CoTAPc–MWCNTs modified surface gave better catalytic responses with a catalytic rate constant of $2.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, apparent electron transfer rate constant of $0.073 \text{ cm}^2 \text{ s}^{-1}$, and a limit of detection of $2.8 \times 10^{-7} \text{ M}$. Scanning electrochemical microscopy (SECM) surface characterization (topography and reactivity) further gave proof the better catalytic performance of the sequential drop dry CoTAPc–MWCNTs modified surface.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Metallophthalocyanines (MPcs) have attracted attention in recent years due to their fascinating chemical and optical properties. Their applications range from health, electronics and traditional uses such as in dyes and pigments [1–4]. MPcs have proved useful in the electrocatalysis of analytes such as 2-mercaptoethanol, hydrazine, L-cysteine and amitrole [5–8], when electroactive central metals such as cobalt, iron, nickel and manganese are used [5]. MPc complexes have been used to modify electrodes by several methods such as self-assembled monolayer, electropolymerization and dip or drop dry [5]. The use of phthalocyanines in the presence of carbon nanotubes for the detection of various analytes has been reported [9–13]. Both single walled (SWCNTs) and multi walled (MWCNTs) carbon nanotubes (alone in the absence of MPc complexes) have been employed for the detection of analytes [14].

Glassy carbon electrodes have been modified with carbon nanotubes (CNT) through adsorption or chemical linking [9–13]. Since the method of modifying the electrode surface is crucial in influencing the electron transfer processes, this work gives a comparative study of drop drying a premixed MPc and MWCNTs solution

against the sequential drop dry CoTAPc–MWCNTs modified surface, whereby a drop of MWCNTs is placed on the GCE surface, followed by the addition of a drop of MPc on top of the MWCNTs layer. We show that the sequential drop dry approach which is reported in this work for the first time, gives improved electrocatalysis. SWCNT have been explored more extensively than MWCNTs for electrode modification [9–13]. Advantages of MWCNT over SWCNT were demonstrated for applications in electronic devices and preparation of nanocomposites [15]. Furthermore, electrical and mechanical properties of SWCNT can change when functionalized due structural defects as a result of C–C bond breakages during chemical processes whereas the intrinsic properties of MWCNTs can be preserved during surface modification since it is only the outer wall which is exposed to chemical modifiers, hence this work explores MWCNTs. Also MWCNTs are cheaper than SWCNTs due to synthetic methods. Cobalt tetraaminophthalocyanines (CoTAPc) is employed due to its well-known electrocatalytic behaviour [6]. L-Cysteine is employed as a test molecule since CoTAPc complexes show good electrocatalytic behaviour for this analyte [6].

2. Experimental

2.1. Materials

L-Cysteine, aluminium oxide and bulky multiwalled carbon nanotubes (MWCNTs) were obtained from Sigma–Aldrich, pH

* Corresponding author.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

4 buffer tablets were from Saarchem. N,N-dimethylformamide (DMF) was obtained from Merck, Germany and was distilled before use. Aqueous solutions of L-cysteine in pH 4 buffer were prepared using millipore water from Milli-Q Water Systems (Millipore Corp. Bedford, MA, USA, conductivity range = 0.055–0.294 $\mu\text{S}/\text{cm}$). CoTAPc was synthesized according to a reported method [16].

2.2. Equipment

A Princeton Applied Research potentiostat/galvanostat Model 263A was used for all cyclic voltammetry (CV) and chronoamperometry (CA) studies. A three electrode electrochemical cell comprising of a glassy carbon electrode (GCE, geometric area = 0.071 cm^2) as the working electrode, Ag|AgCl (3 M KCl) as reference electrode, and a platinum wire as the counter electrode was employed. Electrochemical impedance spectroscopy (EIS) studies were performed using an Autolab Potentiostat PGSTAT30 equipped with GPES software version 4.9. Scanning electrochemical microscopy (SECM) experiments were carried out with the Uniscan Instruments SCV 370, employing a three electrode cell with platinum SECM micro-tip, a platinum wire counter electrode, and a Ag|AgCl reference electrode. The approach curves and images were obtained using 25 μm and 15 μm diameter SECM tips, respectively. Scanning electron microscopy (SEM) images were obtained using a TESCAN Vega TS 5136LM Electron microscope.

2.3. Electrochemical methods

The GCE was polished on a Buehler-felt pad using alumina (10 μm), washed with millipore water, sonicated for 5 min in millipore water and rinsed again with millipore water before each use. CoTAPc and the MWCNTs were separately dissolved in distilled DMF and dispersed through ultrasonication for 5 min. The GCE was modified by the drop-dry method, whereby (i) a drop of the 1 mM CoTAPc mixed with a drop of 0.5 mg/mL MWCNTs was placed on the GCE and allowed to dry {represented as CoTAPc-MWCNT (premixed)} or (ii) drop of 0.5 mg/mL MWCNTs was allowed to dry on GCE, followed by a drop of 1 mM CoTAPc {represented as CoTAPc-MWCNT (sequential)}. Experiments were also performed where CoTAPc was employed in the absence of MWCNTs. The drop size was fixed at 10 μL for all the solutions added onto the electrodes. All solutions were purged with argon gas for 15 min to drive out oxygen before each cyclic voltammetry analysis, and the atmosphere of argon was maintained throughout the period of analysis.

3. Results and discussion

3.1. Characterization of modified electrodes

As stated above MWCNT have been used for the detection of analytes [14]. The aim in this work is to determine the influence of the MWCNT (due to conductive nature) on the catalytic behaviour of CoTAPc. Hence the MWCNTs were not acid functionalized.

3.1.1. Cyclic voltammetry

Fig. 1 shows comparative CVs for the bare and modified glassy carbon electrodes obtained in the presence of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple.

The CVs shown in Fig. 1 represent the second scans of the multiple scans performed. The peaks for the first scans were not well defined, and the rest of the scans were almost the same as the second scans. Peak currents for the modified surfaces (Fig. 1b and c) are several times higher than the bare glassy carbon electrode. However, noteworthy from these CVs for modified surfaces is the higher anodic and cathodic peak currents when the drops of MWCNTs and

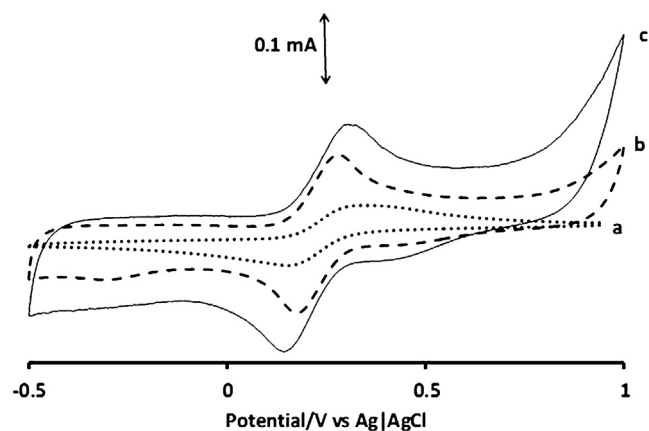


Fig. 1. Comparative cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 1 M KCl using bare GCE (a), CoTAPc-MWCNTs (premixed) (b), and CoTAPc-MWCNTs (sequential) (c). Scan rate, 100 mV/s.

CoTAPc are added separately (Fig. 1c, CoTAPc-MWCNT (sequential)) on glassy carbon electrode than when premixed (Fig. 1b, CoTAPc-MWCNT (premixed)). Thus, CoTAPc-MWCNT (sequential) shows that better electron transfer properties. This is due to the fact that catalysis occurs on the CoTAPc (which should be the top layer) with the bottom layer (MWCNTs) providing transmission of electrons. Furthermore, the capacitive/nonfaradaic currents for (Fig. 1c) are much higher than those for (Fig. 1b), an indication of strong interaction between the modified surfaces and the bare glassy carbon electrode. The anodic to cathodic peak (ΔE) separation was however larger for CoTAPc-MWCNT (sequential) at 150 mV compared to CoTAPc-MWCNT (premixed) at 71 mV, suggesting better electron transfer kinetics for latter even though it shows lower currents. However, by considering SEM images (Fig. 2) we can observe that sequential modification procedure has more exposed bare surface unlike the premixed modified surface which is completely covered. These bare areas are also exposed to the redox mediator hence can contribute to anodic/cathodic peak currents. Therefore peak currents are a result of two influences i.e. modified parts (fast electron transfer) and bare parts (slow electron transfer), leading to peak broadening and widening of peak potential separation. It is clear that despite having some unmodified parts for the sequential treatment, we still have better catalytic currents and sensitivity. This makes the sequential treatment a better procedure to be employed for fabrication of a sensor platform. The reverse where CoTAPc was the bottom layer and MWCNTs was the top layer was found to give very weak catalytic behaviour and was not explored further.

3.1.2. Scanning electrochemical microscopy (SECM)

SECM was employed to probe the conducting behaviour of the modified surfaces. Fig. 3 shows changes in tip current as the ultramicro electrode (UME) tip approaches the substrate in a feedback mode experiment in the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox mediator.

When a sufficiently positive potential is applied to the tip, the oxidation of Fe^{2+} to Fe^{3+} occurs, and the rate is governed by the diffusion of Fe^{2+} to the UME tip surface. When the tip is closer to a conductive substrate surface, the Fe^{3+} diffuses to the substrate where it is reduced back to Fe^{2+} [17,18]. This results in additional flux of Fe^{2+} to UME tip and hence the observed increases in tip current (positive feedback) for bare glassy carbon plate and the modified surfaces. The tip currents for the CoTAPc-MWCNT (sequential) modified surface (Fig. 3d) are higher than the premixed surface modification (Fig. 3c). This is the same trend observed for the anodic peak currents in cyclic voltammetry. The approach

Download English Version:

<https://daneshyari.com/en/article/186070>

Download Persian Version:

<https://daneshyari.com/article/186070>

[Daneshyari.com](https://daneshyari.com)