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Synthesis and characterization of electrocatalytic conjugates of tetraamino cobalt (II) phthalocyanine and single wall carbon nanotubes

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ABSTRACT

In this paper we report on the synthesis and characterization of electrocatalytic conjugates of tetraamino cobalt (II) phthalocyanine and single walled carbon nanotubes (CoTAPc–SWCNT-linked) for use as electrode surface modifiers. FTIR, UV–vis and Raman spectroscopies were used to ascertain the chemical linkage between CoTAPc and SWCNT while cyclic voltammetry and rotating disk electrode voltammetry were used to assess the electrocatalytic efficiency of the linked product towards the oxidation of 2-mercaptoethanol. The CoTAPc–SWCNT-linked-GCE demonstrated very good catalytic efficiency relative to CoTAPc–SWCNT-mixed-GCE, CoTAPc-GCE and f-SWCNTs-GCE (functionalised SWCNT). CoTAPc–SWCNT-linked-GCE gave a sensitivity of 0.2 μA/μM and a limit of detection (LOD) of 1.2×10^{-7} M for 2-mercaptoethanol (2-ME) at pH 4.

1. Introduction

The use of metallophthalocyanines (MPcs) in the fabrication of electrochemical sensors evolved from their unique physico-chemical, electronic and electrocatalytic properties [1]. Like MPcs, carbon nanotubes (CNTs) have very good physico-chemical and electronic properties which make them ideal in fabricating efficient electrochemical sensors [1]. CNTs are known to provide significant reductions in overpotentials, have large surface area and fast and increased voltammetric responses with little or no observed surface fouling [2,3]. The use of carbon nanotubes mixed with MPcs especially those carrying a cobalt centre has been reported to promote electron transfer processes in electrocatalysis [2–4]. Electrodes modified with single walled carbon nanotubes (SWCNT) mixed with MPc (without chemical binding) were found to be stable for analyses [5] and CoPc and SWCNT were found to have synergistic effect on each other in terms of reactivity towards the detection of hydrazine [2]. In this work we report on SWCNTs chemically coordinated to cobalt tetraamino phthalocyanine (Fig. 1a) and employed in the detection of 2-mercaptoethanol (2-ME). Chemical coordination of ZnPc to CNTs has been reported [6,7] using SWCNT which has been functionalised with 4-(2-trimethylsilyl)ethynylaniline. In this work we employ SWCNT which have been functionalised by simple acid treatment. CNTs have been coordinated to MPc molecules and attached to pre-formed SAMs using elaborate methods [3,8–10]. Chemical coordination of cobalt (II) tetraamino phthalocyanine (CoTAPc) to SWCNT has been reported [11], the coordination was confirmed by electrochemical methods. In this work, we use UV–vis, infrared and Raman spectroscopies in addition to electrochemical methods to characterize the CoTAPc attachment to acid functionalised SWCNT. Chemical coordination of cobalt (II) tetraamino phthalocyanine (CoTAPc) to SWCNT was found [11] not to enhance the catalytic activity towards nerve agents (dimethylaminoethanethiol, DMAET and diethylaminoethanethiol, DEAET) when compared to the CoTAPc mixed with SWCNT (without a chemical bond) [11]. In this work we show that an increase in activity is observed for the detection of 2-ME when CoTAPc is linked with SWCNT (represented as CoTAPc–SWCNT-linked, Fig. 1b) and then adsorbed on glassy carbon electrode (GCE). The activity of CoTAPc–SWCNT-linked was compared with that of functionalised SWCNT (represented as f-SWCNT), CoTAPc, CoTAPc mixed with SWCNT without a chemical linkage (represented as CoTAPc–SWCNT-mixed).

Electrochemical detection of thiol-derived substances is an important field of research as thiol can be present as contaminants in fuels and biological fluids and they may be useful as markers of food deterioration. It has been reported that modified electrodes using cobalt phthalocyanine derivatives show substantial electrocatalytic activity for the electro-oxidation of thiols such as 2-mercaptoethanol by lowering particularly the overpotential of the electrochemical processes [1]. 2-ME oxidation has been reported extensively and it leads to formation of 2-hydroxyethyl disulphide [1]. The electrocatalytic oxidation of 2-ME has been done predom-

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