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Electroanalysis of thiocyanate using a novel glassy carbon electrode modified by aryl radicals and cobalt tetracarboxyphthalocyanine

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Abstract

Electrochemical grafting of 4-nitrobenzenediazonium tetrafluoroborate onto a glassy carbon electrode (GCE) results in the formation of a nitrophenyl radical, which reacts with the surface to form a covalent bond (grafting) and results in a nitrophenyl modified electrode. The nitro group is electrochemically reduced to a NH_2 group. Cobalt tetracarboxyphthalocyanine (CoTCPc) complex is then attached to the NH_2 group using 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) as coupling agents. The new CoTCPc modified electrode was characterized using cyclic voltammetry and then employed for the catalytic oxidation of thiocyanate.

Keywords: Cobalt tetracarboxyphthalocyanine; Thiocyanate; Aryl radical; Cyclic voltammetry; 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide; *N*-Hydroxysuccinimide

1. Introduction

The deliberate alteration of electrode surfaces, through the incorporation of an appropriate surface modifier, may solve electroanalytical problems whilst forming the basis for new analytical applications and different sensing devices [1]. Chemically modified electrodes may improve analytical applications [2–5] by accelerating electron transfer reactions or allowing preferential accumulation.

Glassy carbon is popular as an electrode material [1] due to its excellent mechanical and electrical properties, wide usable potential range, relatively reproducible performance (depending largely on solution purity and electrode pre-treatment [6]) and low cost [3] in comparison to Au or Pt electrodes. However, glassy carbon electrode (GCE) fabrication is difficult due to its hardness and fragility, limiting its use to the dimensions and forms obtained commercially [7]. Also, as glassy carbon has some amorphous characteristic, it is not always homogenous [7]. Oxidation of carbon surfaces results in oxygen functional groups (e.g. carboxy or hydroxyl) [8–11]. The precise nature of these oxygen functionalized groups has proven problematic to study, aggravated by carbon surface corrosion [12–14]. It is consequently necessary to develop convenient and efficient modification techniques for the augmentation of glassy carbon surfaces.

Metallophthalocyanines (MPcs) exhibit a series of oxidative and reductive electron transfer processes and hence may be used as versatile electron relays for the activation of redox processes [15,16] when immobilized onto electrode surfaces. Immobilization of MPcs on electrodes by polymerization or by the formation of self-assembled monolayers results in reproducible thin films. However, their formation requires the synthesis of ring substituted MPc complexes, which is very time consuming [17–19]. Methods for electrode modification using readily available MPc complexes are thus being developed. For example formation of self-assembled monolayers (SAMs) of simple MPc complexes onto pre-formed SAMs on gold have been reported [20,21]. In this work we present a new approach for the modification of a glassy carbon electrode (GCE) using a simple MPc complex, cobalt tetracarboxyphthalocyanine (CoTCPc, Fig. 1). A glassy carbon electrode is first modified by grafting of an aryl radical from nitrobenzenediazonium tetrafluoroborate (**1**, Scheme 1) [22], followed by reduction of the NO_2 group to NH_2. The CoTCPc, synthesized according to literature meth-

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