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Self-assembled monolayers (SAMs) of cobalt tetracarboxylic acidchloride phthalocyanine covalently attached onto a preformed mercaptoethanol SAM: A novel method

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Abstract

A feasible method of fabricating phthalocyanine sensor was developed by covalent attachment of cobalt tetracarboxylic acidchloride phthalocyanine (CoTCACIPc) onto a preformed 2-mercaptoethanol (2-ME) self-assembled monolayer (SAM) modified gold electrode (designated as CoTCACIPc-2-ME-SAM). The surface concentration of the CoTCACIPc was found to be 4.58×10^{-10} mol/cm^2. The sensor gave a linear response to L-cysteine over the concentration range 0.28–20 μM with a detection limit of 5×10^{-7} M and best response time of 2 s.

Keywords: Cobalt phthalocyanine; Mercaptoethanol; Self-assembled monolayer; L-Cysteine; Gold

1. Introduction

Metallophthalocyanine (MPc) complexes are still amongst the most studied complexes as heterogeneous catalysts and there has been a considerable attention in immobilizing MPc molecules onto electrode surface with the aim of developing chemical sensors. Such sensors can then be used to monitor (i.e. detect and quantify) molecules, which are of biological, pharmaceutical and environmental importance, such as sulfur containing molecules (e.g. cysteine and 2-mercaptoethanol) [1–8]. MPc complexes containing cobalt (Co) metal center, have in particular been employed successfully as electrocatalysts [9–13]. The uses of MPc complexes as heterogeneous catalysts require their immobilization onto electrodes as thin films. Methods which have been employed for immobilization include self-assembled monolayer (SAM) formation on gold [1–3,14–16].

Self-assembled monolayers represent an incredible means of fabricating stable, easily controllable ultra-thin solid films onto gold or silver metal surfaces [14–18]. In the past, SAMs have been fabricated by coating Au electrodes with thiol-derivatized MPc or other thiol complexes [2,3,19]. However, thiol-derivatized phthalocyanines which may be used for the formation of self-assembled monolayers are amongst the least reported MPc complexes in literature despite their rich electrochemical properties. This is because the synthesis of these complexes is time consuming, tedious and requires expensive and toxic chemical reagents. We have recently reported [20] on the preparation of MPc SAMs by attaching iron phthalocyanine (FePc) complexes (via axial ligation) to preformed 4-mercaptopyridine SAM, thus avoiding the synthesis of thiol-derivatized MPc. To our knowledge, there have been no reports on CoPc ultra-thin films immobilized onto gold electrode via ring coordination onto a preformed thiol-SAM.

In this work, cobalt(II) tetracarboxylic acidchloride phthalocyanine was covalently (via ring coordination) attached onto a preformed 2-mercaptoethanol (2-ME) SAM on gold electrode (represented as CoTCACIPc-2-ME-SAM). To probe the analytical applications of this electrode as a possible electrochemical sensor, we carried out an analysis on its ability to electrocatalytically oxidize and detect a biologically important molecule, cysteine. Cysteine has been widely studied due to its importance in biological systems. It acts as a key extracellular reducing agent, it is also a critical substrate for protein synthesis and rate-limiting precursor for glutathione and taurine synthesis [21].

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