

Surface electrochemistry of iron phthalocyanine axially ligated to 4-mercaptopyridine self-assembled monolayers at gold electrode: Applications to electrocatalytic oxidation and detection of thiocyanate

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Abstract

Surface electrochemical behaviour of a self-immobilised iron phthalocyanine (FePc) ultrathin film, via axial ligation reaction, onto a preformed 4-mercaptopyridine self-assembled monolayer on gold electrode has been described. Electrochemical evidence for the sensor clearly suggested surface-confined, flat “umbrella”-oriented and densely-packed monolayer film structure. The proposed electrochemical sensor exhibited good catalytic activity towards the oxidation of thiocyanate in pH 4.0 medium over a linear range of three decades of concentration (ca. 10^{-6} – 10^{-3} mol dm⁻³) with a detection limit in the order of $\sim 10^{-7}$ mol dm⁻³. The sensor exhibited useful potential for the analysis of thiocyanate in human urine and saliva samples. The advantageous properties of this type of electrode as a sensor for thiocyanate lie in its ease of fabrication, excellent catalytic activity, stability, sensitivity and simplicity.

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1. Introduction

Iron phthalocyanine (FePc) (Fig. 1a) holds special place to phthalocyanine researchers; first, because it was the first metallophthalocyanine (MPc) complex to be discovered by accident in 1928 [1–3] and, second, because of the fact that FePc and its complexes have continued to prove themselves as excellent catalysts for various chemical and electrochemical reactions [1,4–13]. Most of the applications of FePc complexes, and indeed other transition MPc complexes as heterogeneous catalysts, require the use of phthalocyanines as thin films. Research on efficient fabrication of thin films of phthalocyanines has continued to show some steady

growth because of the great potential applications in materials science for electronic, photovoltaic and chemical sensing devices and as ideal models for electron transfer and electrocatalytic reactions [1–3,13–17]. The established strategies for obtaining chemically modified electrodes based on phthalocyanine and related macrocycles include the composite techniques [6,18], dip-dry [19], drop-dry [20,21], spin-coating [16,17], electropolymerisation [22–26] and more recently self-assembly method [14–17,27–31]. The self-assembled monolayer (SAM) approach has the advantage over other techniques in that it can form very stable, well-packed and highly ordered ultrathin solid films on coinage metals such as gold and silver [32–35].

The emergence of self-assembling technique triggered the growing interest in the synthesis of phthalocyanine-linked alkythiols for the fabrication of self-assembled

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