

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 NH₂ group. Cobalt tetracarboxyphthalocyanine (CoTCPC) complex is then attached to the NH₂ 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.

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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 (MPc) 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 MPc 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 NO₂ group to NH₂. The CoTCPC, synthesized according to literature meth-

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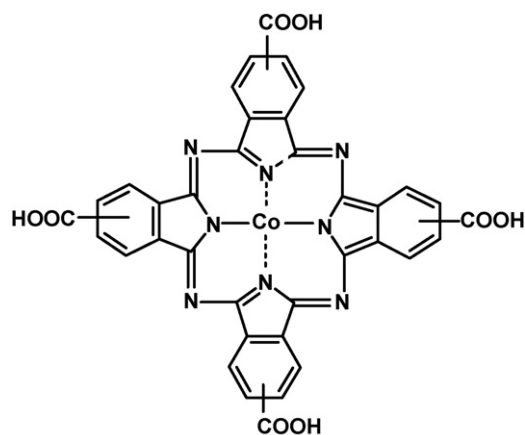
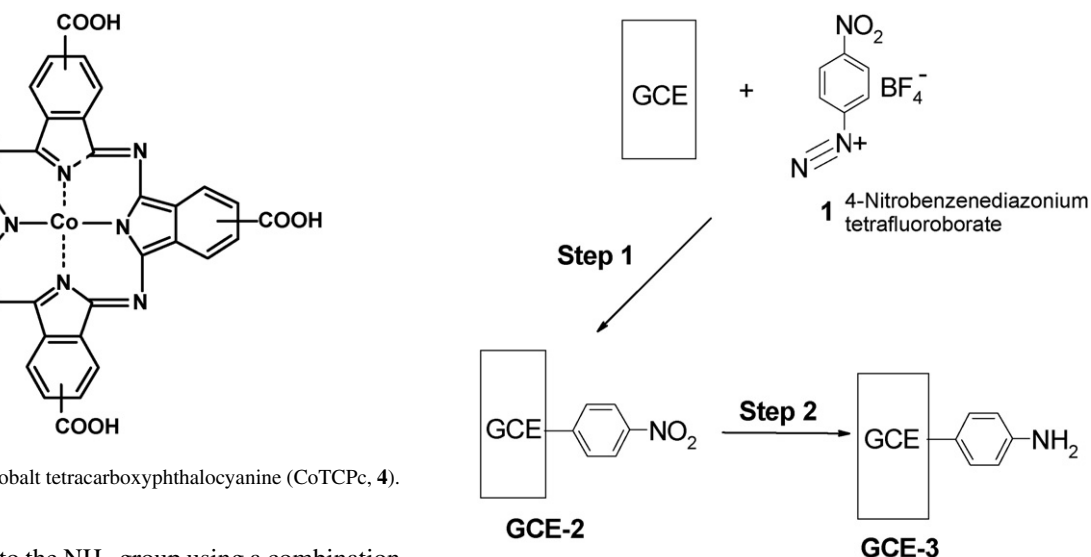


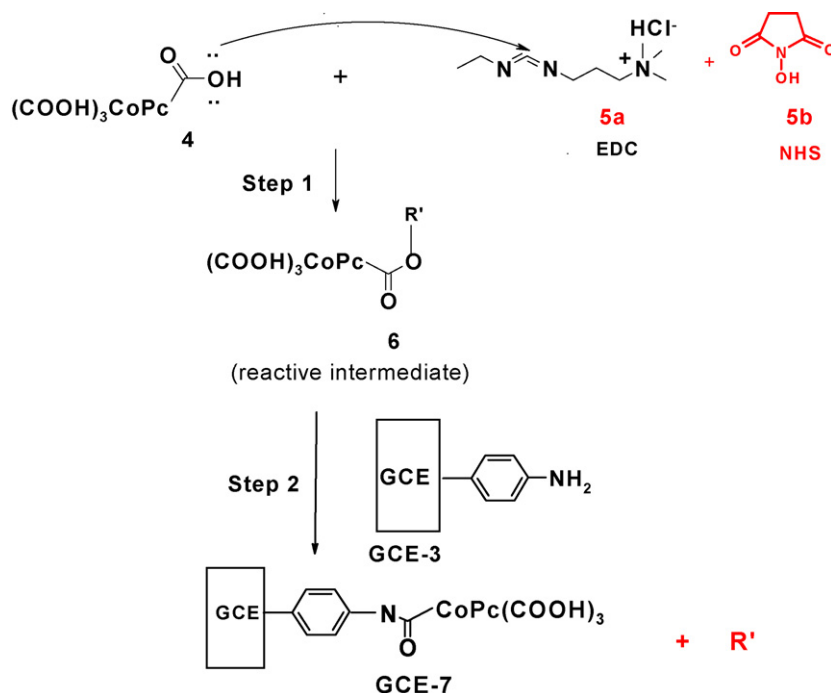
Fig. 1. Molecular structure of cobalt tetracarboxyphthalocyanine (CoTCPC, 4).

ods [23], is then attached to the NH_2 group using a combination of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) as coupling agents, Scheme 2. This work represents the first report of the coordination of a metallophthalocyanine (MPc) to an electrode pre-modified with aryl radicals. MPc complexes (especially CoPc derivatives) are excellent electrocatalysts for many analytes. The most effective methods of electrode modification employed using MPc complexes include electropolymerization and the formation of self-assembled monolayers, both requiring synthesis of derivatised MPc species, which as stated above are time consuming. The method presented in this work provides a new way of forming a stable electrode with readily available MPc complexes without the need for complicated and lengthy synthesis.



Scheme 1. Aryl radical modification of a glassy carbon electrode. GCE = glassy carbon electrode.

The CoTCPC functionalized GCE was used for the electroanalysis of thiocyanate. Thiocyanate is a vital biological and environmental molecule [24–27]. Medically, thiocyanates interfere with thyroxine synthesis in the thyroid gland thereby hindering iodine uptake by the thyroid gland and thiocyanate levels are used to detect the extent of cigarette smoking [25,26]. Environmentally, thiocyanate levels are used to monitor HCN (related chemical of thiocyanate) from fire atmospheres. Thiocyanate is harmful to aquatic life. The detection of thiocyanate is therefore important and hence in this work CoTCPC functionalized GCE is used to electroanalyze thiocyanate.



Scheme 2. Diagrammatic representation of carboxylic acid group (of 4) activation by EDC and NHS (5), followed by reaction with an amine on GCE-3 and then the formation of GCE-7. GCE = glassy carbon electrode. NHS = *N*-hydroxysuccinimide. EDC = 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide.

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