



Synthesis, characterization and application of monocarboxy-phthalocyanine-single walled carbon nanotube conjugates in electrocatalysis

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ABSTRACT

In this paper we report on the synthesis, characterization and use of monocarboxy-phthalocyanine-single walled carbon nanotube conjugates in the electrocatalysis of amitrole and diuron. UV-Vis, FTIR and XRD spectroscopies were used in the characterization of cobalt(II)-tris(benzyl-mercapto)-mono(carboxyphenoxy)-phthalocyanine conjugates (CoMCPC-PA-SWCNT(linked)), while AFM was used to show changes in surface morphologies of the modified electrodes. Cyclic voltammetry and chronoamperometry were used for the electrocatalytic oxidation of amitrole and diuron on the modified glassy carbon electrode. The catalytic rate constants for amitrole and diuron were found to be 1.83×10^6 and $1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The linear range for both was 1.0×10^{-5} – $2.0 \times 10^{-4} \text{ M}$, with sensitivities of 5.10 and $3.70 \text{ A mol}^{-1} \text{ L cm}^{-2}$ for amitrole and diuron, respectively. The limits of detection were estimated to be 0.14 and $0.20 \mu\text{M}$ for amitrole and diuron, respectively, using the 3σ notation.

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1. Introduction

Metallophthalocyanines (MPcs) are 18_v electron complexes that are being used extensively in electro-catalysis [1–4]. Electrode surface modifications with MPcs enhance electron transfer reactions and this could be achieved through adsorption [1], electrodeposition [5] and electropolymerization [6]. These electrode modifiers lower the potentials of redox processes at the electrode|solution interface [7]. Functionalizing MPcs with appropriate groups like carboxylic, hydroxyl and amino groups allows for further derivatization, for example with single walled carbon nanotubes (SWCNTs) carrying extendable functional groups.

Carbon nanotubes (CNTs) are chemically functionalized to provide a higher degree of fine tuning of their chemical and physical properties, including further derivatization and improved solubility [8–11]. Their conductivity and reactivity is a consequence of their electronic properties and chemical functionalization, and this plays an important role in electrochemistry [12–16]. Sidewall functionalization with amines has been reported before [17,18]. Both terminal and sidewall functionalization provide sites for further derivatization with other molecules like phthalocyanines [8].

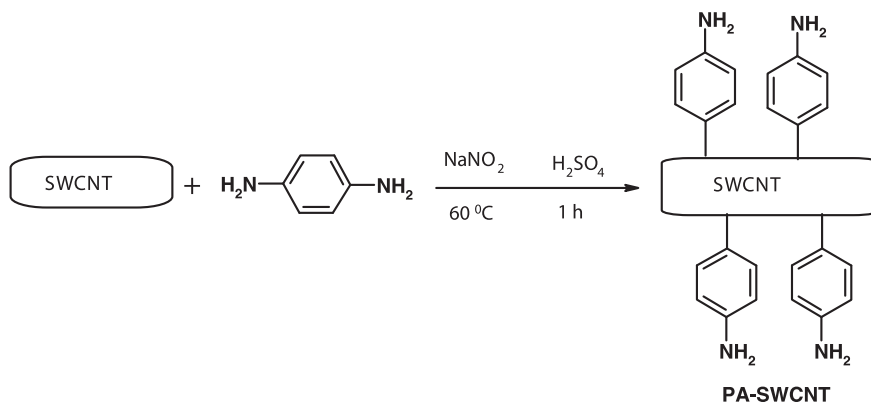
Chemically linking MPcs to CNTs [19–22] is known to improve electro-catalysis.

In this paper we report on the phenyl-amine functionalization of SWCNT (PA-SWCNT, structure shown in Scheme 1) according to a literature method [18] and chemically linking them to cobalt(II)-tris(benzyl-mercapto)-mono(carboxyphenoxy)-phthalocyanine (CoMCPC), a low symmetry molecule (structure shown in Scheme 2) to give CoMCPC-PA-SWCNT (possible structure shown in Scheme 3). Symmetrically substituted MPcs have been linked to CNTs before [19–22], but linking to unsymmetrically monofunctionalized phthalocyanines produces nano-structures of well defined size that provide good alignment on the electrode surface. There are very limited studies of SWCNT linked to low symmetry phthalocyanines due to the difficulties in the synthesis of these complexes [17,23,24]. The synthesis of CoMCPC is reported for the first time in this work. The large surface areas provided by modification of electrodes with nano-structures provide more sites for the electron transfer processes to occur. The presence of the aryl thio groups in CoMCPC lowers the redox potentials of the cobalt center because of their electron donating nature [25].

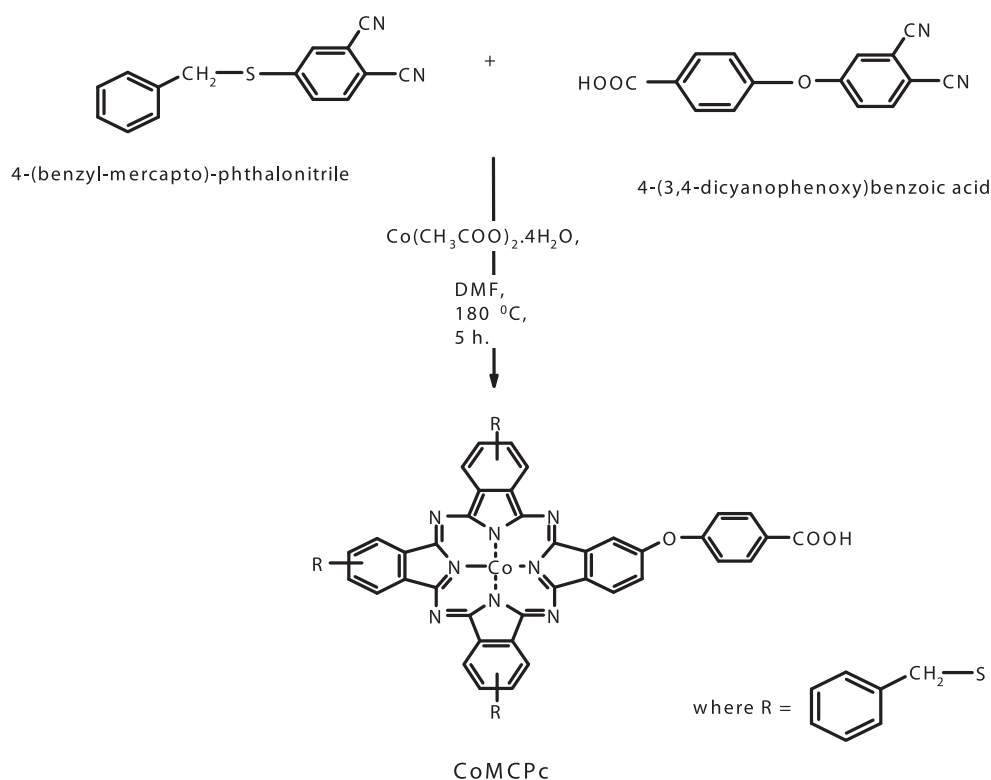
The performance of these complexes as electrocatalysis was studied for the electrochemical characterization of diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and amitrole (3-amino-1,2,4-triazole). Amitrole and diuron are non-selective herbicides that are persistent in soils and water, with the former inhibiting the carotenoid biosynthesis [26]. Electrochemical methods have been employed for the detection of diuron [27,28], however

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Scheme 1. Phenylamine (PA) sidewall functionalisation of SWCNTs.



Scheme 2. Synthetic route to CoMCPc.

passivation of the electrode surface due to the deposition of polymeric products has been observed [27,29]. The use of CoMCPc-PA-SWCNT(linked) for electrochemical characterization of amitrole and diuron is reported in this work.

2. Experimental

2.1. Chemicals and reagents

Amitrole, diuron, 1,4-benzene diamine (BDA), sodium nitrite, single walled carbon nanotubes (SWCNTs, 0.7–1.2 nm in diameter and 2–20 μm in length) and pH 4 buffer tablets were obtained from Aldrich, SOCl_2 was obtained from Merck. Dimethyl-formamide (DMF) and tetrahydrofuran (THF) were from Merck and were freshly distilled and dried before use. Aqueous solutions were prepared using Millipore water from Milli-Q Water Systems (Millipore Corp., Bedford, MA, USA, conductivity range = 0.055–0.294 $\mu\text{S}/\text{cm}$). All other chemicals and reagents were of analytical grade and were

used as received. Stock solutions (2×10^{-3} M) of amitrole and diuron were prepared by dissolving the pesticides in methanol. The syntheses of 4-(benzyl-mercapto)-phthalonitrile and 4-(3,4-dicyanophenoxy)benzoic acid [30,31] have been reported.

2.2. Equipment

Voltammetric and chronoamperometric data were recorded using a Princeton Applied Research potentiostat/galvanostat Model 264 equipped with Electrochemistry PowerSuite software. A three electrode electrochemical cell comprising of glassy carbon electrode (GCE) as the working electrode (area = 0.071 cm^2), platinum wire (Pt) as a counter electrode and a silver|silver chloride wire (Ag|AgCl) as a pseudo-reference electrode was used. Atomic force microscopy (AFM) images were recorded in the non-contact mode in air with a CP-11 Scanning Probe Microscope from Veeco Instruments (Carl Zeiss, South Africa) at a scan rate of 1 Hz. Shimadzu UV-2550 spectrophotometer and Perkin Elmer FTIR spectrometer

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