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Electrochemical, microscopic and spectroscopic characterization of benzene diamine functionalized single walled carbon nanotube-cobalt (II) tetracarboxy-phthalocyanine conjugates

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ABSTRACT

In this paper we report on the synthesis and characterization of 1,4-benzene diamine (BDA) functionalized single walled carbon nanotubes linked to cobalt (II) tetracarboxy-phthalocyanine. The characterization of the conjugate was through UV–vis, FTIR and X-ray diffraction (XRD) spectroscopies and by transmission electron microscope (TEM) and electrochemical methods. The conjugate is used for the electrochemical characterization of diuron. The catalytic rate constant for diuron was 4.4×10^3 M^{-1} s^{-1} and the apparent electron transfer rate constant was 18.5×10^{-6} cm s^{-1}. The linear dynamic range was 1.0×10^{-5}–2.0×10^{-4} M, with a sensitivity of ~0.42 A mol^{-1} L cm^{-2} and a limit of detection of 0.18 μM using the 3δ notation.

1. Introduction

Metallophthalocyanines (MPcs) have versatile chemical and physical properties that can be tailor made through varying the substituent on the phenyl rings. MPcs carrying an electro-active metal centre have good electrocatalytic properties [1]. These electron transfer mediators lower the potentials of redox processes at the electrode|solution interface [2]. Substitution at the peripheral and non-peripheral positions with groups like amino, hydroxyl and carboxyl provide sites for the coordination of phthalocyanines to other electro-active species like carbon nanotubes. Chemically linking MPcs to single walled carbon nanotubes (SWCNTs) [3–5] and multi-walled carbon nanotubes (MWCNTs) [6] is known to improve electro-catalysis.

Single walled nanotubes are one-dimensional nanowires that are either metallic or semiconducting and readily accept charges which they in turn transport along their tubular axis [7]. Carbon nanotubes (CNTs) possess other special exploitable physical and chemical properties, including high chemical stability [7]. They can be functionalized with carboxylic and amino groups in order to increase their ability to chemically link with other compounds [8,9] and also increase their solubility [10]. On their own carbon nanotubes are good electro-catalysts for a variety of analytes [11], but their performance can be greatly enhanced through physical [12] and chemical combination with MPcs, especially those carrying an electro-active metal centre. Improved catalytic activity and reduced overpotentials have been reported when CNTs are physically [12] and chemically [13] combined with MPcs. Cui and Guo [6] used dispersed platinum nanoparticles on 1,4-benzene diamine functionalized multi-walled carbon nanotubes for the oxidation of methanol. Thus in this paper we report on the linking of 1,4-benzene diamine functionalized single walled carbon nanotubes (BDA-SWCNT) to cobalt (II) tetracarboxy-phthalocyanine (CoTCPc), Schemes 1 and 2. The phenyl-amine groups that are attached to SWCNT provide a platform for the further coordination of SWCNTs to the carboxylated phthalocyanines. CoTCPc contains the electron withdrawing carboxylic acid groups, that are easily converted to the acid chloride moiety, which is a suitable precursor for chemically linking the MPc to the amine functionalized SWCNT. The 1,4-benzene diamine functionalized single walled carbon nanotubes (BDA-SWCNT) donate electrons to the MPcs, thereby increasing the electron density on the phthalocyanine. The sound electron transfer properties of the single walled carbon nanotubes (SWCNTs) coupled with the good electronic properties of the MPc do serve as the basis for the good electron transfer efficiencies of chemically linked conjugates. The conjugate (represented as

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