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Insights into the surface and redox properties of single-walled carbon nanotube—cobalt(II) tetra-aminophthalocyanine self-assembled on gold electrode

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Abstract

This paper describes for the first time the electrochemical properties of redox-active self-assembled films of single-walled carbon nanotubes (SWCNTs) coordinated to cobalt(II)tetra-aminophthalocyanine (CoTAPc) by sequential self-assembly onto a preformed aminoethanethiol (AET) self-assembled monolayer (SAM) on a gold electrode. Both redox-active SAMs (Au-AET-SWCNT and Au-AET-SWCNT-CoTAPc) exhibited reversible electrochemistry in aqueous (phosphate buffer) solution. X-ray photoelectron spectroscopy (XPS) confirmed the appearance on the gold surface of the various elements found on the SAMs. Atomic force microscopy (AFM) images prove, corroborating the estimated electrochemical surface concentrations, that these SAMs lie normal to the gold surface. Electrochemical impedance spectroscopy (EIS) analyses in the presence of $[Fe(CN)_6]^{3-/4-}$ as a redox probe revealed that the Au-AET-SWCNT-CoTAPc showed much lower (∼10 times) electron-transfer resistance (R_{et}) and much higher (∼10 times) apparent electron-transfer rate constant (k_{app}) compared to the Au-AET-SWCNT SAM. Interestingly, a preliminary electrocatalytic investigation showed that both SAMs exhibit comparable electrocatalytic responses towards the detection of dopamine in pH 7.4 phosphate buffer solutions (PBS). The electrochemical studies (cyclic voltammetry (CV) and EIS) prove that SWCNT greatly improves the electronic communication between CoTAPc and the Au electrode surface.

Keywords: Cobalt(II)tetra-aminophthalocyanine; Single-walled carbon nanotube; Self-assembled monolayer; XPS; AFM; Cyclic voltammetry; Impedance spectroscopy; Dopamine

1. Introduction

The transition metallophthalocyanine (MPc) complexes have shown themselves as versatile macrocyclic organometallic complexes with applications in several technologically relevant areas [1–3], notably in the design and fabrication of electrochemical sensors where their use has escalated over the last two decades because of their excellent physico-chemical, electronic and electrocatalytic properties [4–6]. Like the MPc complexes, carbon nanotubes (CNTs), single-walled carbon nanotubes (SWCNTs) or multi-walled (MWCNTs), exhibit unique physico-chemical and electronic properties ideal for constructing efficient electrochemical sensors [7–11]. Thus, rational integration of these two remarkable π-electron species may revolutionize their applications in a plethora of areas, especially in electrocatalysis and nanofabrication of molecular electronic and sensing devices. Without doubt, most of the potential applications of MPc and CNTs in electronic, photoconductive and heterogeneous electrocatalysis and sensing devices will require their use as thin films. Self-assembly represents a more efficient technique for fabricating electrodes based on CNT [8,12,13] or MPc [14–20] thin films compared to such other thin film formation methodologies such as drop-dry and spin coating.

Self-assembly may simply be described as a spontaneous, coordinated chemical reaction of individual molecular

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