Electrochimica Acta 53 (2008) 8051–8057

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrooxidation of hydrazine catalyzed by noncovalently functionalized single-walled carbon nanotubes with CoPc

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ARTICLE INFO

Article history:
Received 27 March 2008
Received in revised form 15 May 2008
Accepted 31 May 2008
Available online 19 June 2008

Keywords:
Cobalt phthalocyanine
Hydrazine
Single-walled carbon nanotube
Atomic force microscope
Cyclic voltammetry
Electrochemical impedance spectroscopy

ABSTRACT

We report on the electrooxidation of hydrazine catalyzed by single-walled carbon nanotube (SWCNT) functionalized with cobalt phthalocyanine (CoPc) which shows that the presence of the single-walled carbon nanotubes enhances the catalytic activity of the CoPc itself without any change in the reaction mechanism. A synergistic effect, in terms of reactivity when the new nanocomposite material was adsorbed on the GC electrode, was observed. The obtained hybrid electrodes were tested under hydrodynamic conditions, showing two different oxidation processes, which suggest the presence of two different types of active sites on the electrode surface catalyzing the reaction. Electrochemical impedance spectroscopy (EIS) analyses in the presence of $[Fe(CN)_6]^{3-/4-}$ as a redox probe revealed that the GC/SWCNT + CoPc showed much lower electron-resistance (R_{et}) confirming the synergistic effect of the composite mentioned above. Atomic force microscopy (AFM) images showed the clear differences in surface roughness for each film, confirming the different compositions of the hybrid electrodes used in this study.

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1. Introduction

It is well known that the electrooxidation of hydrazine is highly sensitive to the nature of the surface used [1–8]. Actually, the reaction can be considered as an inner sphere reaction since a strong interaction between a nitrogen atom and an active site is expected to occur before or when the electron-transfer (ET) takes place [9]. On the other hand, it is well known that cobalt phthalocyanine (CoPc) exhibits a high catalytic activity for many reactions [9–14] including the electrooxidation of N_2H_4 [2,4,8,9]. Additionally, CoPc can be adsorbed very strongly on graphite and carbon-based electrode materials at a monolayer level [1,2,5,6] to form the chemically modified electrodes.

Carbon nanotubes (CNTs) [15] are a relatively new kind of carbon nanostructure materials possessing properties such as high electrical conductivity, high surface area, good chemical stability and significant mechanical strength [16–20]. These properties of CNTs have been used to promote the electron-transfer reaction when applied as electrode materials in electrochemical devices [21–24]. This is in part due to the reported significant reductions in overpotentials, large surface area, increase in the magnitude of voltammetric signals and little or no observed surface fouling. In addition, this kind of carbon material has been used to disperse and stabilize electron-transfer mediators forming chemically modified carbon nanotube electrodes showing an enhanced reactivity for reactions that benefit from electrocatalysis [25–29]. Although CNTs have been noncovalently functionalized by using metalloporphyrins [30] and metallophthalocyanines [31,32] to promote electron-transfer process in electrocatalysis, there are no reports on the effects of CNTs on the reaction mechanism for the analytes studied.

In this work, we studied the effect of single-walled carbon nanotubes (SWCNTs) noncovalently functionalized with CoPc on the kinetics of hydrazine oxidation. For this proposal, it was imperative to functionalize SWCNT in noncovalent ways, *via* π–π interaction, to preserve the sp^2 nanotube structure and thus their electronic characteristics. Potentiodynamic studies, electrochemical impedance spectroscopy and atomic force microscopy measurements were employed in order to explain the effect of CNTs.

2. Experimental

2.1. Materials and reagents

CoPc and single-walled carbon nanotubes (SWCNT, 0.7–1.2 nm in diameter and 2–20 μm in length) were purchased from Aldrich.

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0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.05.083