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Comparative electrocatalytic studies of nanocomposites of mixed and covalently linked multiwalled carbon nanotubes and 4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninato cobalt(II)

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ABSTRACT

Electrocatalytic behavior of 4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninato cobalt(II) (CoPyPc) when mixed or covalently mixed to multiwalled carbon nanotubes (MWCNTs) is reported. Infra-red spectroscopy was used to confirm amide linkage of the covalently linked nanocomposite. Rotating disk electrode (RDE) and cyclic (CV) voltammetry studies were used for the electrochemical characterization of the prepared phthalocyanine and MWCNT nanocomposite. The electrocatalytic effects of the nanocomposites of the cobalt phthalocyanine derivative were then investigated towards L-cysteine oxidation using both RDE and CV experiments, and the electrocatalytic performance of the covalently linked cobalt phthalocyanine-MWCNT was found to be superior over the mixed nanocomposite.

1. Introduction

Metallophthalocyanines are well known electrocatalysts [1,2]. There is a wealth of research on the electrocatalytic behavior of cobalt phthalocyanine and its derivatives for many reactions including nitrite oxidation [3], oxygen reduction reaction [4], reduction of carbon dioxide [5] and sulfhydryl oxidation [6], among others. On the other hand, multiwalled carbon nanotubes (MWCNTs) have been found to have good conductivity [7–10], and have been used in electrocatalysis of a wide range of analytes such as in oxygen reduction reaction [11], ethanol and methanol oxidation [12,13], and hydrogen peroxide sensing [14,15]. The nanometer size of MWCNT provides good dispersion and high surface area features. This is very important in lowering the catalyst loading hence making MWCNT to be suitable electrocatalytic support systems for improving performance of metallophthalocyanines for applications in the fabrication of miniaturized sensor platforms. Furthermore, the interest in using nanocomposites containing phthalocyanines and MWCNTs in this work is influenced by the fact that a variety of nanocomposites have also been reported to enhance electrocatalytic responses in many applications such as glucose sensing [16], NADH oxidation [17], oxygen reduction reaction in fuel cells [18], lithium battery applications [19], etc.

Therefore, the key objective of this work is to combine MWCNT with a cobalt phthalocyanine derivative to modify solid electrode surfaces with an overriding intent of facilitating some rather sluggish reactions occurring at the bare surfaces. We fabricated our nanocomposites through two processes; (i) functionalizing MWCNT with carboxylic acid functional groups and covalently linking them to the amine terminals of 4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninato cobalt(II) (CoPyPc, Scheme 1) and (ii) dispersing the CoPyPc onto MWCNT through π–π interactions. The synergistic electrocatalytic performance of the nanocomposites produced from the two processes is then systematically compared side-by-side. We have reported on the electrocatalytic behavior of CoPyPc in the presence of MWCNT when both are adsorbed onto glassy carbon electrode (GCE) [20]. Adsorption is a fast and easy method. However, its limitation is that it is not often reproducible. A Pc is covalently linked to MWCNT for the first time in this work. The route for covalently linking and mixing MWCNT–COOH and CoPyPc is shown in Scheme 1. CoPyPc was chosen due to the presence of a number of NH_2 groups for linking to acid functionalized MWCNTs. Co tetraamino phthalocyanine (CoTAPc) has been covalently linked to single walled carbon nanotubes (SWCNTs) for electrocatalytic applications [21,22]. CoTAPc has also been electropolymerized onto MWCNTs [23], but there are no reports on its covalent coordination to MWCNTs. The preference for the use of CoPyPc in this work instead of the commonly used CoTAPc is as a result of the bulkier substituents for the former which reduces aggregation. MWCNTs are preferred over SWCNTs in this work since studies have shown that the presence

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