

Electrode Modification Using Alkyne Manganese Phthalocyanine and Click Chemistry for Electrocatalysis

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Abstract: In this work, azidobenzene diazonium salt is grafted onto a glassy carbon electrode (GCE) followed by clicking of manganese tetrahexynyl phthalocyanine for the electrocatalysis of hydrazine. The GCE was first grafted via the in situ diazotization of a diazonium salt, rendering the GCE surface layered with azide groups. From this point, the 1,3-dipolar cycloaddition reaction, catalyzed by a copper catalyst was utilized to 'click' the manganese tetrahexynyl phthalocyanine to the surface of the

grafted GCE. This new platform was then characterized using cyclic voltammetry (CV), scanning electrochemical microscopy (SECM) and X-ray photoelectron spectroscopy (XPS). Based on the cyclic voltammetry calibration curve of electrocatalysis for hydrazine, the clicked Mn phthalocyanine electrode proved to be an effective sensor with a sensitivity of $27.38 \mu\text{A mM}^{-1}$ and the limit of detection (LoD) of 15.4 pM which is a great improvement compared to other reported sensors for this analyte.

Keywords: Manganese Phthalocyanine · Electrografting · Click Chemistry · Electrocatalysis · Hydrazine

1 Introduction

Many diazonium salts have been grafted onto electrodes [1,2]. The grafting of 4-azidobenzene diazonium salt (with a terminal alkyne group) allows for the attachment of alkynyl containing complexes through "Sharpless click" reaction [3–6]. The Sharpless "click" reaction term was first used in 2001 [5]. A good example of a click chemistry reaction is the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to give triazole linkages [5,6]. The reaction occurs in the presence of Cu(I) catalyst. In this work an alkynyl containing manganese phthalocyanine is used to modify a glassy carbon electrode grafted with an azide group using the click reaction.

Metallophthalocyanines (MPcs) have shown good electrocatalytic behaviour for the detection of analytes such as hydrazine, amitrole, and L-cysteine [7]. Manganese as a central metal for MPc, was chosen since it has various oxidation states (I–IV) which should result in favorable electrocatalytic behavior especially for reactions requiring multi-electron transfer. In addition, MnPc derivatives have shown improved electrocatalytic oxidation of hydrazine [7], which is used as a test analyte in this work. Hydrazine is heavily used in chemical industry, and has been implicated as a carcinogen and is readily absorbed through the skin [8].

Alkynyl substituted MPc complexes are known [9–13], and the synthesis of Mn tetrakis(5-hexyn-oxy) phthalocyanine (complex **1**, Scheme 1) employed in this work has been reported [13]. However, apart from our recent report on alkynyl substituted FePc [14,15], there are no reports on electrode modification using click chemistry and alkynyl Pcs. This is the first time that an alkynyl MnPc is employed. The combination of grafting and click chemistry offers a covalent attachment of MPcs onto the electrode, resulting in a stable layer, hence it is employed

in this work. The modified electrodes are characterized by various techniques including X-ray photoelectron spectroscopy, scanning electrochemical microscopy, and various electrochemical methods.

2 Experimental

2.1 Materials

Millipore water was obtained from Milli-Q Water Systems (Millipore Corp. Bedford, MA, USA). Alumina ($\leq 10 \mu\text{m}$), dimethylformide (DMF), dimethyl sulfoxide (DMSO), copper(I) complex ($\text{Cu}(\text{PPh}_3)_3\text{Br}$), tetrabutyl ammonium tetrafluoroborate (TBABF_4), trimethylamine and hydrazine monohydrate were purchased from Sigma Aldrich and used as they are received. Acetonitrile (ACN) was obtained from Minima. Iron ferricyanide and iron ferrocyanide were obtained from Unilab and used as received. Dichloromethane (DCM) was obtained from B&M Scientific. 4-Azidobenzene diazonium salt was synthesized as reported in literature [16].

2.2 Equipment

An Autolab PGSTAT30 electrochemical workstation (equipped with GPES software version 4.9) was used for cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). Scanning electrochemical microscopy (SECM) experiments were conducted using Uniscan equipment, model 370 and

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