



Characterization of electrodes modified by one pot or step by step electro-click reaction and axial ligation of iron tetracarboxyphthalocyanine



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ARTICLE INFO

Article history:

Received 30 July 2014

Received in revised form 5 September 2014

Accepted 5 September 2014

Available online 8 September 2014

Keywords:

Electropolymerization

Electro-click

iron tetracarboxyphthalocyanine

hydrazine

electrocatalysis

ABSTRACT

The modification of the glassy carbon electrode (GCE) was carried out using two methods. The first method is simultaneous electropolymerization and electro-click followed by immersion into a solution of dimethyl formamide (DMF) containing FeTCPC. The second method is step by step whereby electropolymerization is carried out first followed by electro-click and then immersion into a DMF solution containing FeTCPC. From the electrochemical characterization, it was observed that the second route (step by step method) was the best as indicated by the ferricyanide studies, cyclic voltammetry and scanning electrochemical microscopy). In the electrooxidation of hydrazine, we obtained a potential of 0.26 V. Of interest were the detection limit of 6.4 μM and the catalytic rate constant of $2.1 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This shows that the sensor can be used for the electrooxidation of hydrazine.

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1. Introduction

There has been progress in the use of the copper (I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction to form triazoles [1–3]. Of interest is the fact that electrochemists have also adopted the technique for the modification of various electrode surfaces [2,4–12]. The general reaction condition for the CuAAC click reaction involves the use of alkyne or azide functionality, copper salt (mostly CuSO_4) and ascorbic acid or sodium ascorbate. The copper salt is the source of Cu catalyst, whereas ascorbic acid or sodium ascorbate functions to reduce Cu^{II} to Cu^{I} . Most electrochemists used biased potentials in the range -0.2 V to -0.5 V [8,10]. The rationale being these potentials are roughly 300 mV negative of the $\text{Cu}^{\text{III/I}}$ standard potential, ensuring that $\text{Cu}(\text{I})$ is formed at the electrode surface.

Rydzek et al. proposed a new strategy in which they performed a click reaction in a one pot synthesis whereby the glassy carbon electrode was modified by a simultaneous electropolymerization and electro-click (SEEC) [12]. The one pot synthesis offers many advantages which include its efficiency and reliability. In this paper, our aim is to compare one pot (SEEC) with the step by step electrode modification (electropolymerization followed by electro-click). Our group have reported on the introduction of an

unsubstituted iron phthalocyanine through axial ligation [4,5] following CuAAC click reaction involving ethynylpyridine. In the reported work [4,5], the glassy carbon electrode was modified by grafting of 4-azidobenzenediazonium salt followed by click chemistry with ethynylpyridine, whereas this work used electropolymerization followed by electro-click reaction. Electropolymerization (compared to grafting) offers versatility in terms of a wide variety of molecules which can be electropolymerized, hence it is employed in this work.

In this work, we use iron tetracarboxyphthalocyanine (FeTCPC) since it is a known electrocatalyst towards the detection of hydrazine [13]. Hydrazine was employed as the test analyte because it is a carcinogenic and hepatotoxic substance which affects the liver and the brain glutathione [14]. Metallophthalocyanines are good electrochemical catalysts. This is due to the accessibility of a range of oxidation states on the Pc unit itself or on the central metal incorporated into the phthalocyanine [15]. To the best of our knowledge this is the first time a phthalocyanine molecule is used for hydrazine electrooxidation on electrodes modified by step by step (electropolymerisation followed by click chemistry) or SEEC.

2. Experimental

2.1. Chemicals and reagents

All the chemicals used in this study were of analytical grade and used without further purification. Hydrazine sulphate,

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