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Research Paper

Exploiting Click Chemistry for the Covalent Immobilization of Tetra (4-Propargyloxyphenoxy) Metallophthalocyanines onto Phenylazide-Grafted Gold Surfaces

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ABSTRACT

In this study, tetra-(4-propargyloxy)phenoxy phthalocyanines (MTPrOPhOPc) were covalently immobilized as thin films onto gold surfaces via click reaction. The gold electrode surfaces were pre-functionalized with phenylazide (Au-PAz) thin film using in-situ diazonium generation followed by electrografting. Copper (I) catalyzed alkynyl-azide cycloaddition (CuCAAC) reaction was used to covalently immobilize the MTPrOPhOPcs onto the gold electrode surfaces to form Au-PAz-MTPrOPhOPc. The MTPrOPhOPcs were further studied for their electrocatalytic and electroanalytical properties towards the detection of hydrogen peroxide. Au-PAz-MTPrOPhOPc exhibited good reproducibility and stability in various electrolyte conditions. Electrochemical and spectroscopic surface characterization of the functionalized gold electrode surfaces confirmed the presence of the phenylazide and MTPrOPhOPc thin monolayer films. The excellent electroanalysis of hydrogen peroxide with the limit of detection (LoD) and limit of quantification (LoQ) in the μM range was obtained. The electrocatalytic reduction peaks for H_2O_2 were observed at −0.37 V for Au-PAz-Mn(OAc)TPrOPhOPc and −0.31 V for Au-PAz-CoTPrOPhOPc when Ag|AgCl pseudo-reference electrode was used. The Au-PAz-Mn(OAc)TPrOPhOPc and Au-PAz-CoTPrOPhOPc gold electrode surfaces showed good sensitivity and reproducibility towards the electrocatalytic reduction of hydrogen peroxide in pH 7.4 phosphate buffer solution.

1. Introduction

Conventional methods such as spectroscopy [1–5], chromatography [6] and electrochemistry [7–9] are amongst the various techniques used for hydrogen peroxide detection. The drawback of using the spectroscopic and chromatographic techniques is the bulky instrument required and hence confining these techniques to laboratory use only. The electrochemical technique is an analytical instrument of choice and this is due to its simplicity, the potential for miniaturization and can be mass produced for ease of portability. Amongst the advantages, the portability allows for point-of-care applications and field-testing [10]. The most recent studies on electrochemical detection of hydrogen peroxide employ biological molecules [7], electroactive synthetic materials [11], inorganic nanomaterials [12] in the sensor development. Extensive research has been conducted on the use of enzymes, that are known to contain heme moiety, as a redox active center for the electrocatalytic or enzymatic reductants of H_2O_2 to H_2O [13]. During the design and applications, enzyme-based sensors require careful control of their immobilization as they can denature and lose activity [7]. Researchers have therefore embarked on the development of synthetic electroactive-based electrochemical sensors that are highly stable and cheaper than enzymes.

Metallophthalocyanines (MPcs) [11,14–16] and their nanostructured conjugates [17,18] have found research interest and are promising substitutes for the costly enzyme-based sensor in the electrochemical detection of hydrogen peroxide. These materials have high thermal stability, excellent electrocatalytic properties and are biologically compatible [19]. Recent studies for the electrochemical detection of H_2O_2 using MPc-modified gold electrodes have shown promising results [11,18,20–23]. There is, however, a continued need to investigate different chemical strategies for immobilizing MPcs onto gold electrode surfaces and thus forming stable thin monolayer films that will allow their applications in various conditions. This is a quest of researchers in this investigation. The current research studies have shown that exploring the various chemical strategies can afford the immobilization of the MPcs as thin monolayer films [20–23] and also as

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