



Research Paper

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



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ARTICLE INFO

Article history:

Received 15 August 2017

Received in revised form 16 September 2017

Accepted 19 September 2017

Available online 20 September 2017

Keywords:

Metallophthalocyanines
terminal alkynyl
phenylazide
gold electrodes
hydrogen peroxide

ABSTRACT

In this study, tetra-(4-propargyloxy)phenoxy phthalocyanines (MTPPrOPhOPc) 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 MTPPrOPhOPcs onto the gold electrode surfaces to form Au-PAz-MTPPrOPhOPc. The MTPPrOPhOPcs were further studied for their electrocatalytic and electroanalytical properties towards the detection of hydrogen peroxide. Au-PAz-MTPPrOPhOPc 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 MTPPrOPhOPc 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)TPPrOPhOPc and -0.31 V for Au-PAz-CoTPPrOPhOPc when Ag|AgCl pseudo-reference electrode was used. The Au-PAz-Mn(OAc)TPPrOPhOPc and Au-PAz-CoTPPrOPhOPc gold electrode surfaces showed good sensitivity and reproducibility towards the electrocatalytic reduction of hydrogen peroxide in pH 7.4 phosphate buffer solution.

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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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nanomaterials conjugates [18]. In this work, we report the use of CuCAAC “Click chemistry” to immobilize the recently synthesized tetra 4-(propargyloxy)phenoxy metallophthalocyanines (MTPrO-PhOPc, M = H₂, Co, and Mn) with the terminal alkyne (C≡CH) onto the gold surface, as shown in Fig. 1. The method of immobilization and the characterization of the formed thin films will be studied. The phthalocyanines bearing 4-(propargyloxy)phenoxy substituents will be studied for their formation of stable thin films on gold electrode surfaces and their electrocatalytic properties towards the detection of hydrogen peroxide. The combination of electrografting and click chemistry is useful for the formation of stable thin films of electroactive complexes [24] and biomolecules onto electrode surfaces [24–27].

2. Experimental

2.1. Chemicals and reagents

Potassium ferricyanide [K₃Fe(CN)₆], potassium ferrocyanide [K₄Fe(CN)₆], 98% sulfuric acid (H₂SO₄), sodium chloride (NaCl), potassium chloride (KCl), 4-azidoaniline and 30% hydrogen peroxide were obtained from Sigma-Aldrich (South Africa). Potassium hydroxide pellets (KOH), absolute ethanol (EtOH), potassium dihydrogen phosphate (KH₂PO₄) and disodium hydrogen phosphate (Na₂HPO₄) were purchased from SAARCHEM and used as received. Copper (I) iodide (CuI) was purchased from SAARCHEM. CuI was purified following the procedure in the literature [28], stored in dry phosphorus pentoxide (Sigma-Aldrich) desiccator and was stable during the chemical reaction. Acetonitrile (ACN), dimethylsulfoxide (DMSO), dimethylformamide (DMF), sodium nitrite (NaNO₂) and methanol were purchased from Merck Chemicals. The gold-coated quartz crystals (AuCQC, Gold/Chrome O100RX1) were purchased from Stanford Research System (ThinkSRS.com) were modified and used for the XPS analysis. DMF was distilled and stored dry over molecular sieves before use. All aqueous solutions were prepared using double distilled water or ultra-pure water with the resistivity of 18 MΩ.cm (at 25 °C) obtained from a Milli-Q Water Purification System purchased from Millipore Corporation. Electrocatalysis and electroanalysis of H₂O₂ were performed in freshly prepared phosphate buffer saline solution (PBS) pH 7.4. Phosphate buffer saline solution (0.010 M pH 7.4) was prepared following the reported literature [29] and using suitable amounts of Na₂HPO₄, KH₂PO₄ and chloride salts, dissolved in ultra-pure (Milli-Q) water. The unmetallated (H₂) and metallated cobalt and manganese tetra 4-(propargyloxy)phenoxy phthalocyanines, H₂TPrO-PhOPc (**1**), CoTPrO-PhOPc (**2**) and Mn(OAc)TPrO-PhOPc (**3**) recently synthesized [30] and will be used to form stable thin monolayer films.

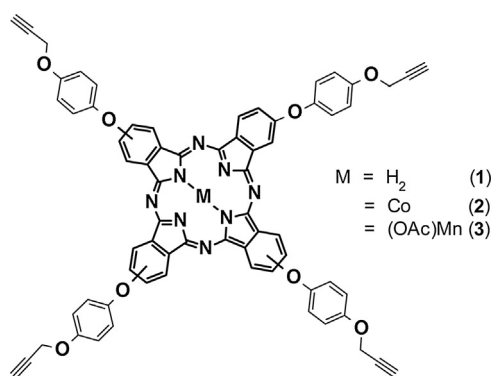


Fig. 1. Chemical structure of the unmetallated (**1**, H₂) and metallated cobalt (**2**, Co) and manganese (**3**, Mn) tetra 4-(propargyloxy)phenoxy phthalocyanines.

2.2. Apparatus and Instrumentations

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed on an AUTOLAB PGSTAT302N potentiostat/galvanostat work station interfaced to a proline desktop computer equipped with a 1.10 version NOVA software. A conventional three-electrode system was used, with the working electrode (WE) either a bare or modified gold disc (Au, with 0.8 mm radius). The geometric surface area of the Au electrode was calculated to be 0.0201 cm². The platinum wire was used as a counter electrode (CE) while the reference electrode (RE) was either the silver-silver chloride (Ag|AgCl) pseudo-reference or silver-silver chloride in 3.0 M solution of sodium chloride (Ag|AgCl, 3.0 M NaCl). The pseudo Ag|AgCl reference electrode is related to Ag|AgCl (3.0 M NaCl) by 0.015 V. The EIS experiments were recorded in the frequency range between 10 kHz to 100 MHz at a formal potential of E_{1/2} of the [Fe(CN)₆]^{3-/4-} redox couple for a bare gold electrode and with an amplitude 5 mV rms sinusoidal modulation. Measurements of pH were conducted using a Thermo Scientific Orion Star A329 Portable pH/ISE/conductivity/RDO/DO meter. X-ray photoelectron spectroscopy (XPS) was used to measure and analyze the data. The experimental set-up and specification are as previously reported [31]. The Vision processing data reduction software (Kratos Analytical Ltd) was used for data analysis and curve fitting. Curve fitting was performed using Gaussian-Lorentzian peak shape after performing a linear background correction. The raw data is shown as black markers with the fitted signal shown as red solid line. The synthesized peaks were shown as different coloured solid lines. The NIST XPS Database, Version 4.1 was used for assigning of the synthesized or deconvoluted peaks [32].

2.3. Electrode pre-treatment and modification with thin monolayer films of MTPrO-PhOPcs (1–3)

A clean gold electrode surface was achieved by following the established procedures [33], which involved first polishing with a 2400 grit SiC-emery paper and followed by mirror finish on a Beuhler felt pad using an aqueous slurry of alumina (1 μm, 0.3 μm, and 0.05 μm). The electrode was then ultrasonicated for 5–10 min in absolute ethanol to remove residual alumina particles trapped on the surface. The polished gold electrode was then chemically treated by etching for about two minutes in a “Piranha” solution of 3:1 (v/v) (30% H₂O₂/98% H₂SO₄). The gold electrode was then rinsed with ultrapure Milli-Q water followed by ethanol. The cleaned electrode was dried in a stream of argon. The chemical treatment with “Piranha” solution serves to remove the organic contaminants on the gold electrode surface. The cleanliness of bare gold electrode surface was finally established by placing the electrode in 0.50 M H₂SO₄ and scanning the potential between –0.5 and 1.0 V (versus Ag|AgCl pseudo-reference or Ag|AgCl in 3.0 M NaCl) until reproducible scans were obtained. The clean gold surface was modified with MTPrO-PhOPc (**1–3**) using the method shown in Scheme 1. The first step in the formation of thin films involved the pre-modification of gold electrode surfaces with the thin film of the phenylazide functional groups, represented as Au-PAz. This was accomplished via (i) an in-situ generation of 4-azidophenyl diazonium in the solution containing 0.50 M HCl and 1.0 M NaNO₂ and (ii) 4-azidophenyl diazonium was then electrochemically reduced to form 4-azidoaryl radicals which was grafted onto the gold electrode surface at high negative potentials beyond the radical reduction peak potential.

The immobilization of the H₂TPrO-PhOPc (**1**), CoTPrO-PhOPc (**2**) and Mn(OAc)TPrO-PhOPc (**3**) was achieved via CuCAAC or “Click” chemical reaction. The CuCAAC reaction works favourably with terminal alkyne (R–C≡CH) of the phthalocyanine substituents

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