



Electrocatalytic behaviour and application of manganese porphyrin/gold nanoparticle- surface modified glassy carbon electrodes

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ABSTRACT

The main purpose of this research was to obtain manganese porphyrin/gold nanoparticle-modified glassy carbon electrodes and to use them for the detection of H₂O₂. Two sets of modified electrodes were prepared by drop-cast deposition of 5,10,15,20-tetra(4-methyl-phenyl)porphyrinato manganese(III) chloride alone and of the same Mn-porphyrin and gold-colloid solution and comparatively characterized by Raman, UV–vis, ellipsometry, AFM and TEM microscopy, XPS and cyclic voltammetry. XPS spectrum recorded for GC_MnP_nAu modified electrode displayed the characteristic signals of gold nanoparticles. The optical parameters have greater values for GC_MnP_nAu in comparison with GC_MnP, due to increasing charge transfer efficiency. The MnP_nAu film mediates the electron transfer between H₂O₂ and GC, evidenced by an increase in the current intensity of the anodic peak, and facilitates the electrochemical regeneration of oxidized H₂O₂ at cathodic potentials. From the cyclic voltammetry experiments a linear relationship between H₂O₂ concentration vs oxidation and reduction currents was observed. The linear dependence between density of current and the square root of the scan rate indicates that the oxidation and reduction processes of H₂O₂ are diffusion controlled. The GC_MnP_nAu modified electrode shows great potential as electrochemical sensor for determination of hydrogen peroxide.

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1. Introduction

Porphyrins and their metallic complexes possessing catalytic and biological properties are widely studied [1] and among these, manganese porphyrins are well-known to act as ionophores in potentiometric sensors [2,3] and other nanoscale devices [4].

The manganese porphyrins deposited on electrodes were reported as efficient catalysts for oxidation of water to molecular oxygen [5], of indole using hydrogen peroxide as a green oxidant [6] in the epoxidation of alkenes [7,8] and in the detection of biomarkers [9] and dopamine neurotransmitter [10].

Abbreviations: MnP, 5,10,15,20-tetra(4-methyl-phenyl)porphyrinato manganese(III) chloride; nAu, gold nanoparticle; GC_MnP, glassy carbon electrode modified with MnP; GC_MnP_nAu, glassy carbon electrode modified with MnP and nAu; n, refractive index; k, extinction coefficient; α, absorption coefficient; ia, anodic waves; ic, cathodic waves; E_{1/2}, half-wave potential.

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Photodegradation of organic compounds in water solutions by means of environment-friendly processes using silica-Mn porphyrin hybrids [11] or TiO₂ samples impregnated with metalloporphyrins is also a topic of large interest [12].

The obtaining of new complex systems based on manganese porphyrin derivatives in association with metallic or carbon based nanoparticles provides improved performance of electrochemical devices [13]. Successful epoxidation of alkenes catalyzed by manganese(III)-tetraphenylporphyrin chloride, immobilized on magnetite nanoparticles [14] or on single/multi wall carbon nanotubes were also reported [15].

In particular, gold nanoparticles [16] are recommended because they can be deposited on the electrode surface, create better conditions to charge transfer and increase the surface area. Besides, the gold surface can be functionalized with metalloporphyrins and due to spherical geometry, void spaces are present that allow efficient mass transfer. Thin films of Co(II) metalloporphyrins deposited on electrodes in the presence of gold nanoparticles found applications as sensors for detection of nitrite anions [17] or in electrocatalytic reduction of O₂ [18].

A synergistic behaviour between gold nanoparticles and manganese(III)meso-tetrakis(pentafluorophenyl) porphyrin proved to be useful for the detection of L-cysteine [9].

Immobilization of porphyrins on gold colloids was also considered in the formulation of photosensitizing materials for photovoltaic cells [19] and for the electrochemical detection of thrombin [20].

A limited number of studies have concerned on electrochemically oxidation processes, but most of these involve manganese porphyrins in the role of mediators in electrocatalytic processes.

Based on our previous investigations [21,22] that involved Mn-porphyrins behaviour in the presence of H₂O₂ and due to the fact that manganese porphyrins are considered among the best oxygen carriers but also taking into consideration that the accumulation of H₂O₂ in mitochondria is correlated with diseases such Alzheimer, Parkinson, Huntington, inclusive cancer [23], our approach is to obtain a manganese porphyrin/gold nanoparticle-modified glassy carbon electrode for the sensitive determination of H₂O₂. This is important because higher concentrations of H₂O₂ than 50 μM are considered as cytotoxic for life [24,25].

In the present work, we prepared and characterized manganese porphyrin/gold nanoparticle-modified glassy carbon electrodes (GC.MnP.nAu). The properties of the GC.MnP.nAu electrodes were studied in comparison to those of GC.MnP and bare glassy carbon electrodes. The GC.MnP.nAu electrodes show great potential as electrochemical sensors for determination of hydrogen peroxide.

2. Materials and methods

2.1. Chemicals

Auric acid (HAuCl₄), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), trisodium citrate, hydrogen peroxide (30% aqueous solution), potassium hexacyanoferrate(III) (K₃Fe(CN)₆), potassium chloride (KCl), potassium nitrate (KNO₃), sodium dihydrogen phosphate (NaH₂PO₄), disodium hydrogen phosphate (Na₂HPO₄) were purchased from Sigma Aldrich and Merck as analytical grade reagents and used without further purification. All solutions were prepared using bi-distilled water.

2.1.1. Obtaining of

5,10,15,20-tetra(4-methyl-phenyl)porphyrinato manganese(III) chloride (MnP)

The porphyrin used in this study (see Fig. A.1 in Supplementary data) was synthesized using modified Adler's method [26] followed by metalation [27].

2.1.2. Synthesis of gold nanoparticles (nAu)

A colloidal solution of gold nanoparticles (nAu) with controlled sizes of gold particles in the narrow range 15–18 nm, was prepared by reduction of HAuCl₄ using citrate following a previously published method [28,17]. The solution turns from yellow to black and then to dark red. Initial concentration of the colloid solution was 0.68×10^{-3} M. During experiments the solution was kept at 5 °C.

2.2. Preparation of the modified electrodes

Prior to each experiment the glassy carbon (GC) surface was mechanically polished using fine grade emery papers (5 and 0.3 μm), cleaned with water and immersed in sulfuric acid (0.5 M). After that, the electrode was successively sonicated in water, acetone and ethanol for 3 min each.

The porphyrin film was formed by drop-casting from a DMF solution containing MnP (1 mM, 3 μL) onto the well cleaned GC surface and left to dry. Then the electrode was rinsed with DMF

and water and left to dry in the dark. The nAu film was formed by drop-casting of the colloidal solution (0.68×10^{-3} M, 5 μL) onto the MnP modified GC electrode and left to dry, followed by rinsing with water.

2.3. Instrumentation

The Raman spectrum was measured by the MultiView-2000 system (Nanonics Imaging Ltd., Israel) and incorporated Shamrock 500i Spectrograph (ANDOR, United Kingdom) at room temperature. A laser wavelength of 514.5 nm was used as the excitation source with 20 s exposure time and 300 mm⁻¹ grating.

UV-vis spectroscopy was performed on a JASCO UV-V-650 spectrometer (Japan) using 1 cm pass cells.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using AMICUS ESCA3400 spectrometer (Kratos Analytical, UK) with an Mg and Al X-ray monochromatic source (1486.6 eV and 1253.6 eV) and a power of operating of 300W (12 kV, 25 mA).

The atomic force microscopic (AFM) measurements were carried out using a Nanosurf® EasyScan2 Advanced Research AFM, in contact mode.

Transmission electron microscopic (TEM) images were obtained using a Titan G2 80–200 (FEI Company) instrument operating at 80 kV. Samples for TEM analysis were prepared on carbon-coated copper grids by placing 2 μL of diluted THF solution of MnP and allowed the solvent to evaporate. A diluted aqueous gold colloidal solution (1:3 v/v, 2 μL) was dropped on top of this film and allowed to dry. The solvents were evaporated under vacuum.

The ellipsometry spectra were recorded with M-2000 (J.A. Woollam Co.) spectroscopic ellipsometer in the wavelength range of 250–1000 nm.

Electrochemical measurements were performed with a VoltaLab PGZ 301 potentiostat (Radiometer Analytical). A three-electrode conventional cell (V=5 mL) with a Pt wire as auxiliary electrode, ESC as reference electrode and glassy carbon (S=0.07 cm²) bare and modified with MnP and nAu as working electrodes was used. All potentials were measured with respect to the SCE electrode. The electrochemical performance of the electrodes was assessed using cyclic voltammetry in 1 M KNO₃ solution and 0.1 M phosphate buffer solution (PBS). The electrocatalysis of hydrogen peroxide was carried out in 0.05 M PBS solutions, pH 7, at a scan rate (v) of 50 mV s⁻¹. The cell was open to the atmosphere.

3. Results and discussion

3.1. STEM, TEM and AFM microscopic characterization

The STEM image of MnP film represented in Fig. 1(a) shows round type porphyrin aggregates around 160 nm and lace type surfaces with fractal borders.

The TEM image of gold nanoparticles, shown in Fig. 1(b) proves the spherical geometry of the gold particles that are present as single particles (with diameters ranging from 15 nm to 18 nm) and in their aggregate form, usually in triads organized in triangles or chain linked structures.

The TEM image of the thin film obtained by consequent deposition of MnP and nAu, represented in Fig. 1(c) evidenced single particles of gold mixed together with large associated particles and a circular mode of aggregation, probably induced by porphyrin substrate. We presume that this behaviour was favoured by electrostatic interaction between MnP charges and redox ability and negatively charged gold surface.

The morphology and geometry of the MnP and MnP.nAu films deposited on GC surface were studied by AFM analysis, as shown in Fig. 2. The 2D AFM image of GC-MnP observed in Fig. 2(a) offers data

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