

# Characterization and electrocatalytic properties of Prussian blue electrochemically deposited on nano-Au/PAMAM dendrimer-modified gold electrode

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## Abstract

Gold electrode was modified with 3-mercaptopropionic acid (MPA) and further reacted with poly(amidoamine) (PAMAM) dendrimer (generation 4.0) then attached the nano-Au to obtain films on which Prussian blue (PB) was electrochemically deposited to afford much wider pH adaptive range, much better electrochemical stability and excellent electrochemical response. The microstructure and electrochemical behavior of Au/MPA/PAMAM/nano-Au/PB electrode were investigated by scanning electron microscopy (SEM) and cyclic voltammetry. The electrochemical response of the Au/MPA/PAMAM/nano-Au/PB-modified electrode for the electrocatalytic reduction of hydrogen peroxide was investigated, and it was found that the sensitivity as well as the corresponding detection limits were improved as compared to the voltammetric response of a Au/PB-modified electrode and Au/MPA/PAMAM/PB electrode. Based on this, a new electrochemical sensor for determination of hydrogen peroxide has been developed.

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## 1. Introduction

Prussian blue (PB) is a prototype of metal hexacyanoferrates with well-known electrochromic (Kulesza et al., 2001), electrochemical (Itaya et al., 1986), photophysical (Kaneko et al., 1985), and magnetic properties (Mingotaud et al., 1999) and potential analytical applications (Karyakin, 2001). Due to its excellent electrocatalysis, PB is widely used as an electron-transfer mediator in the amperometric biosensors (Karyakin et al., 2000, 2002; Katz and Willner, 2004; Derwinska et al., 2003). Recently, PB has been defined as an “artificial peroxidase” because of its analogy with the biological family of peroxidase enzymes, responsible in nature for reduction hydrogen peroxide (Karyakin et al., 2000). The main problem of the chemically modified electrodes reported to date, however, relies on the fact that the electrocatalytic film of PB is stable only at low pH val-

ues (Scharf and Grabner, 1996; Moscone et al., 2001a,b), and therefore, its integrity and activity are seriously compromised by bulk and local changes in pH that often appear as a consequence of electron-transfer events in the interfacial region (Bustos et al., 2005). The pH stability seems to be dependent on the different modes of deposition of PB layer (Ricci and Palleschi, 2005). An increased stability of the PB layer at alkaline pH was observed by adopting a chemical deposition method which was a useful alternative to the most used electrochemical approach for the modification of the electrode surface with PB (Moscone et al., 2001a,b; Ricci et al., 2003b). The greatly enhanced stability of PB layer, which deposited on screen-printed electrodes (SPEs), made possible the practical application of H<sub>2</sub>O<sub>2</sub> sensor even at alkaline pH and with the coupling to an oxidase enzyme (such as glucose oxidase and choline oxidase) having an optimum pH of 8.0 (Ricci et al., 2003a). Other methods, ranging from the use of protective polymers to the use of additives in the deposition buffer, have been proposed to increase the operational stability of PB. In recent years, conducting and non-conducting polymers such as poly(*o*-diaminobenzene) (Lukachova et al., 2002, 2003),

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poly(*o*-phenylenediamine) (Garjonyte and Malinauskas, 1999, 2000), and poly(vinylpyrrolidone) (Uemura and Kitagawa, 2003; Xian et al., 2005) were used to improve the performance of PB layer by providing a better stability. Electropolymerization of 4,4'-bis(butylsulfanyl)-2,2'-bithiophene (Lupu et al., 2002) and *o*-aminophenol (Pan et al., 2004) on a PB-modified platinum electrode resulted in an enhanced reproducibility and stability of the sensor produced. In addition, the additive, tetrabutylammonium toluene 4-sulfonate (TTS) presented in the working solution helped stabilize hexacyanoferrate-modified electrodes (Lin and Shih, 1999). And it was demonstrated that TTS used both in the carrier stream of flow injection analysis or in the buffer used for the electrodeposition of PB markedly improved the stability of the PB layer (de Mattos et al., 2003; Haghghi et al., 2004). Furthermore, an ionic conductor such as Nafion has also provided a higher stability of the PB film (Karyakin et al., 1995).

Dendrimers are highly branched and monodisperse macromolecules with a well-defined three-dimensional and globular structure (Grayson and Frechet, 2001). They have received extensive attention due to their potential applications in the fields of chemical and biomedical sensors (Vogtle et al., 2000; Cagin et al., 2000), microelectronic and biomimetic systems (Tully and Frechet, 2001), adhesion, coating, and membrane chemistry (Tsukruk, 1998), and nanotechnology (Emmrich et al., 2002). Dendrimer molecules possess three basic architectural components: an initiator core (e.g., ethylenediamine), interior layers often called “generations”, which comprise repeating units attached to the initiator core, and the shell which generally consists of functionalized groups attached to the outermost interior layer. Although most of the work with dendrimers has been carried out in solution, these compounds have also been used to modify electrode surface and some recent reports indicate that these materials are capable of increasing the concentration of hydrophobic molecules at the electrode–solution interface, improving in this way the sensitivity as well as the selectivity of certain specific electrochemical reactions. Among various dendrimers, poly(amidoamine) (PAMAM) is the most frequently studied. Godinez and co-researcher modified gold bead electrode with PB containing starburst PAMAM dendrimer to afford mixed and stable electrocatalytic layers which not only showed an improved surface coverage of PB on the dendrimer-modified electrode but also showed an enhanced stability at neutral pH values (Bustos et al., 2005). They also compared the preparation and performance of covalently modified gold electrodes with various generations of PAMAM dendrimers loaded with PB, and developed an amperometric sensors of H<sub>2</sub>O<sub>2</sub> using the dendrimer–PB-modified electrodes (Bustos et al., 2006). Recently, Wu et al. (2007) improved the selectivity and stability of amperometric detection of hydrogen peroxide using PAMAM/PB supramolecular complex membrane as a catalytic layer.

To the best of our knowledge, no study using nano-Au immobilized on PAMAM dendrimer to load with PB has been reported. In this paper, we report the preparation and characterization PAMAM/nano-Au/PB films anchored on 3-mercaptopropionic acid-modified electrode and some preliminary results on the electrocatalytic activity of hydrogen peroxide.

## 2. Experimental

### 2.1. Reagents

Amine terminated G4 poly(amidoamine) dendrimer (PAMAM), 3-mercaptopropionic acid (MPA), and KCl were purchased from Aldrich. *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), gold colloid (20 nm) and FeCl<sub>3</sub> were obtained from Sigma. K<sub>3</sub>Fe(CN)<sub>6</sub> was obtained from Mallinckrodt. Hydrogen peroxide was obtained from Junsei Chemical Co. Ltd. All chemicals used were of analytical-reagent grade, and water (>18 MΩ cm) was obtained from a Millipore Milli-Q purification system.

### 2.2. Apparatus

The cyclic voltammetry (CV) and electrochemical impedance measurements were performed with an Autolab potentiostat 10 (Ecochemie). A three-electrode system used in the measurements consists of a gold electrode or a modified gold electrode as the working electrode, platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All potentials are given with respect to the Ag/AgCl electrode. Scanning electron microscopy (SEM) images were obtained using a Philips XL 30S FEG operated at 10 and 3 kV.

### 2.3. Electrode preparation

Gold electrodes were prepared by electron beam evaporation of 40 nm of Ti followed by 150 nm of Au onto Si(100) wafers. The electrode was cleaned in piranha solution, rinsed with water, and then dried with nitrogen gas. The pretreated electrode was immersed in 1.0 M ethanol solution of MPA (75/25% ethanol/water) for 12 h at room temperature and then washed thoroughly in 75/25% ethanol/water to remove the non-chemisorbed materials. Subsequently, the Au/MPA-modified electrode was immersed in 1.0 mg mL<sup>-1</sup> PAMAM dendrimer solution in presence of 5 mM EDC for 12 h period at room temperature. Thus surface anchoring of dendrimers G4 PAMAM on the thiol-modified gold electrodes was carried out by means of peptidic bond formation using traditional peptide chemistry protocols. After rinsed with distilled water, the Au/MPA/PAMAM membrane electrode was transferred into gold colloid solution for 12 h at 4 °C. Then, the Au/MPA/PAMAM/nano-Au-modified electrode was fabricated. The schematic illustration of the stepwise self-assembly procedure is shown in Fig. 1 (Scheme 1). In order to compare with the electrochemical behavior for different electrodes, three modified electrodes, that is, Au/PB, Au/MPA/PAMAM/PB and Au/MPA/PAMAM/nano-Au/PB electrodes were prepared by the electrochemical deposition of PB. The electrodeposition of PB were achieved by immersing the preprocessed electrode in a carefully deoxygenated (20 min) solution containing 2.5 mM FeCl<sub>3</sub>, 2.5 mM K<sub>3</sub>Fe(CN)<sub>6</sub>, 0.1 M KCl and 0.1 M HCl, followed by a cyclic scan in a potential range of -0.5 to +0.65 V at 50 mV/s for 15 cycles. After deposition, the electrodes were thoroughly washed with double-distilled water, then transferred

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