

Electrocatalytic oxidation and detection of hydrazine at gold electrode modified with iron phthalocyanine complex linked to mercaptopyrindine self-assembled monolayer

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Abstract

Electrocatalytic oxidation and detection of hydrazine in pH 7.0 conditions were studied by using gold electrode modified with self-assembled monolayer (SAM) films of iron phthalocyanine (FePc) complex axially ligated to a preformed 4-mercaptopyrindine SAMs. The anodic oxidation of hydrazine in neutral pH conditions with FePc-linked-mercaptopyrindine-SAM-modified gold electrode occurred at low overpotential (0.35 V versus Ag|AgCl) and the treatment of the voltammetric data showed that it was a pure diffusion-controlled reaction with the involvement of one electron in the rate-determining step. The mechanism for the interaction of hydrazine with the FePc-SAM is proposed to involve the Fe^(III)Pc/Fe^(II)Pc redox process. Using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV), hydrazine was detected over a linear concentration range of 1.3×10^{-5} to 9.2×10^{-5} mol/L with low limits of detection (ca. 5 and 11 μ M for OSWV and CV, respectively). At concentrations higher than 1.2×10^{-4} mol/L the anodic peak potential shifted to 0.40 V (versus Ag|AgCl), and this was interpreted to be due to kinetic limitations resulting from the saturation of hydrazine and its oxidation products onto the redox-active monolayer film. This type of metallophthalocyanine-SAM-based electrode is a highly promising electrochemical sensor given its ease of fabrication, good catalytic activity, stability, sensitivity and simplicity.

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Keywords: Iron phthalocyanine; Mercaptopyrindine; Self-assembled monolayer; Electrocatalysis; Hydrazine; Anodic oxidation

1. Introduction

Metallophthalocyanine (MPc) complexes are a fascinating group of macrocyclic compounds because of their ability to exhibit excellent physico-chemical properties that are essential for various technologically important applications, such as in molecular electronics, photovoltaic devices and electrochemical sensors [1–3]. Hydrazine (N₂H₄) is a powerful reducing agent, which is useful as a fuel in fuel cells [4]. Hydrazine and its derivatives are frequently found in our environment, and are used as essential raw materials and/or intermediates in some industrial preparations such as pesticides, but also suspected to be carcinogenic and mutagenic [5]. A

highly sensitive method is necessary for the reliable measurement of hydrazine. Electro-oxidation of hydrazine, which is an established four-electron process, had been extensively studied with several electrodes modified with MPc (M = Fe, Co, Cu, Mn, Ni, Cr, Zn, VO and Sn) complexes as electrocatalysts [6–19]. FePc (Fig. 1) is known to have a higher electrocatalytic activity towards the oxidation of hydrazine compared to other MPc complexes such as the CoPc and MnPc [7]. It is indicative from literature survey that the construction of MPc-based modified electrodes for the oxidation and/or detection of hydrazine has almost entirely been devoted to the use of CoPc complexes [6–15] with just few reports on FePc and its derivatives [7,16–19]. Furthermore, most of the experiments were performed using cathodic electrochemical measurements and in strong alkaline pH conditions, with little reports on the application of FePc-based electrodes [17,18]

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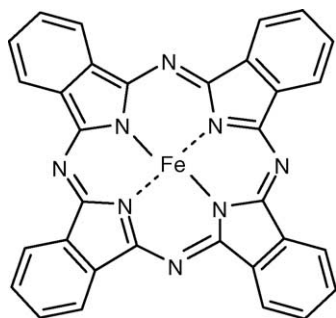


Fig. 1. Molecular structure of iron phthalocyanine (FePc) complex.

and other MPC [10,13,15] in neutral or physiological pH conditions. This is surprising since the anodic electrochemical oxidation and determination of hydrazine in neutral or physiological pH conditions offers certain advantages, for example, no interference from molecular oxygen, which is usually the major limitation in the cathodic determination. Also, strong alkaline ($\text{pH} > 9$) conditions can be disadvantageous to the use of chemically modified electrodes (CMEs) as electrochemical sensors since such harsh conditions ($\text{pH} > 10$) could lead to desorption from the electrode substrates. SAM-modified electrodes in particular easily desorb in alkaline conditions [20–23]. In contrast, most CMEs can easily be employed for analysis in neutral pH conditions. Also, such hydrazine-sensitive MPC-based electrodes were constructed using the traditional electrode modification strategies such as dip-dry [14], drop-dry and electropolymerization [16,19] as well as the composite techniques such as those based on sol-gel-derived carbon electrode [10], carbon-wax [13] and silica-gel [15].

The self-assembled monolayer (SAM) approach is the more modern strategy for the modification of coinage-metal based electrodes such as gold and silver with alkanethiols and their derivatives [20–23]. SAM-modified electrodes have distinct advantages over the traditionally modified electrodes in that very stable, well-packed and highly ordered ultrathin solid films can be quickly formed on the electrode surface. It is these advantages of SAM technique that have resulted to the growing interests in the synthesis of thiol-derivatised metallophthalocyanine complexes [24–28] for the fabrication of self-assembled MPC monolayers (MPC-SAMs) on gold. It is disappointing, however, that the preparation of thiol-derivatised metallophthalocyanine complexes, especially the iron phthalocyanine complexes, is difficult, time-wasting, and requires extensive use of chemical reagents. Thus, it is important to look for less time-consuming and low-cost strategies for the fabrication of MPC-SAM on gold electrodes that would eliminate the need for the synthesis of thiol-derivatised MPC complexes, as shown in this work, by simply using a preformed N-donor ligand SAMs.

In this work, we report on the first example of the electrocatalytic behaviour of a self-assembled monolayer of a FePc complex towards the anodic oxidation and detection of hydrazine in neutral pH conditions.

2. Experimental

2.1. Materials and reagents

4-Mercaptopyridine (MPyr), iron phthalocyanine (FePc) and hydrazine sulfate were obtained from Aldrich. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used to prepare the phosphate pH 7.0 buffer solution. All other reagents were of analytical grade and were used as received from the suppliers without further purification.

2.2. Apparatus

All electrochemical experiments, cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were performed using Bio-Analytical Systems, 100 B/W Electrochemical Workstation. A conventional three-electrode system was used. The working electrode was either bare gold ($r=0.8$ mm, BAS) or gold electrode modified with 4-mercaptopyridine SAM or MPC-linked-4-mercaptopyridine-SAM. A Ag|AgCl wire and platinum wire were used as pseudo-reference and counter electrodes, respectively. The optimised parameters for the OSWV were: step potential 4 mV; square wave amplitude 25 mV at a frequency of 15 Hz. Tap water sample was collected from public tap water in Grahamstown and was analysed on the same day using the OSWV technique. The pH of the tap water was measured as 7.04, hence there was no need for a pH adjustment. A Wissenschaftlich-Technische Werkstätten (WTW) pH 330/SET-1 (Germany) pH meter was used for pH measurements. All solutions were de-aerated by bubbling nitrogen prior to each electrochemical experiment. All experiments were performed at 25 ± 1 °C.

2.3. Electrode fabrication

Electrode fabrication was carried out using a procedure similar to the self-assembly strategies described in the literature [29,30]. Gold electrode ($r=0.8$ mm, BAS) was first polished using aqueous slurries of alumina (<10 μm) on a SiC-emery paper (type 2400 grit), and then to a mirror finish on a Buehler felt pad. The electrode was then placed in ethanol and subjected to ultrasonic vibration to remove residual alumina particles that might be trapped at the surface. Finally the electrode was etched for about 2 min in a hot ‘Piranha’ solution {1:3 (v/v) 30% H_2O_2 and concentrated H_2SO_4 } and then rinsed with copious amounts of ultrapure Millipore water followed by ethanol. The electrode was then rinsed with absolute ethanol and immediately placed into a nitrogen-saturated absolute ethanol solution of 4-mercaptopyridine (1×10^{-3} mol/L) for 1 h at ambient temperature. The mercaptopyridine-modified electrode was thoroughly rinsed in absolute ethanol solution and then immersed in tetrahydrofuran (THF) solution of FePc (1×10^{-3} mol/L) for 4 h at ambient temperature. Upon removal from the depo-

sition solution, the electrode was rinsed with THF and dried in nitrogen atmosphere prior to electrochemical experiments. When not in use, the sensor was stored in nitrogen-saturated buffer solution (pH 4.0) at room temperature.

3. Results and discussion

3.1. Electrode characterisation: surface electrochemistry

The modified electrode was fully characterised using cyclic voltammetric techniques and under anaerobic conditions to avoid the interference of atmospheric oxygen in the cathodic window measurements. The surface electrochemistry of each surface (bare gold, MPyr-SAM-modified gold, and FePc-linked-MPyr-SAM-modified gold surface) exhibited typical characteristics of electrodes surfaces immobilised with different molecules. Fig. 2, for example, compares typical cyclic voltammograms of (a) bare gold electrode, (b) MPyr-SAM on gold electrode, and (c) FePc-linked-MPyr-SAM on gold electrode in pH 4.0 phosphate buffer solution. It can be easily seen that the formation of MPyr-SAM and a typical FePc-linked-MPyr-SAM led to a dramatic reduction of the capacitive charging current of the bare gold electrode, which is a very common phenomenon for thiol-modified gold electrodes. There was no noticeable redox peak at the MPyr-SAM gold electrode within the potential range (between -0.50 and $+0.50$ V versus Ag|AgCl) investigated. Contrary to MPyr-SAM, FePc-linked-MPyr-SAM exhibited a pair of well-defined, quasi-reversible redox peak with potential peak separations (ΔE_p) and half-wave peak potentials ($E_{1/2}$) of approximately 80 and -40 mV (versus Ag|AgCl), respectively. From the well established redox chemistry of FePc and its complexes [31], the reversible redox wave of the FePc-linked-MPyr-SAM ($E_{1/2} \approx -0.04$ V versus Ag|AgCl) is a one-electron process due to the $[\text{Fe}^{\text{III}}\text{Pc}(-2)]/[\text{Fe}^{\text{II}}\text{Pc}(-2)]$. Ideal, surface-confined, diffusionless species are characterised by zero ΔE_p values. Thus, the peak separation of

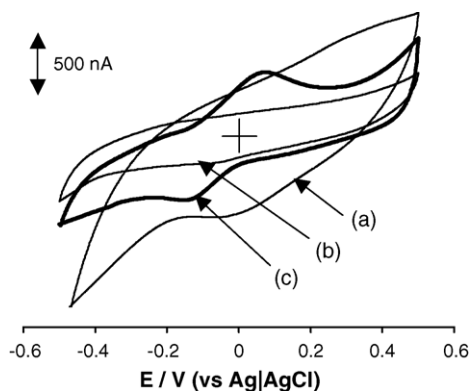


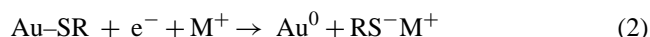
Fig. 2. Cyclic voltammograms of (a) bare gold electrode, (b) MPyr-SAM on gold electrode, and (c) FePc-linked-MPyr-SAM on gold electrode. Electrolyte = pH 4.0 phosphate buffer; scan rate = 25 mV s^{-1} .

80 mV (versus Ag|AgCl) might suggest kinetic limitations or electrostatic interactions of the molecules in the monolayer films. The surface coverage (Γ_{FePc}) was evaluated from the usual equation [32]:

$$\Gamma_{\text{FePc}} = \frac{Q}{nFA} \quad (1)$$

where Q is the electric charge obtained from the background-corrected anodic peak at 25 mV s^{-1} ($\sim 1.35 \times 10^{-7} \text{ C}$), n = number of electron (~ 1), F the Faraday constant (96485 C mol^{-1}) and A the electrode geometric surface area (0.0201 cm^2) and estimated to be ca. $7.0 \times 10^{-11} \text{ mol cm}^{-2}$, indicating a monolayer coverage for an MPc complexes with a flat orientation [33]. A perpendicular orientation could be ruled out since it would have given a much higher surface coverage.

As a further characterisation, we also examined the voltammetric reductive desorption of the bare and modified gold surfaces. It is known [22] that thiolates (RSH) are desorbed from the gold surface by the following reduction process in an alkaline aqueous solution (Eq. (2));



where M^+ cation from the electrolyte is usually included in the desorption equation because the peak is sensitive to the identity of the cation. Fig. 3 is typical cyclic voltammograms of reductive desorption of gold electrodes modified with (a) MPyr-SAM and (b) FePc-linked-MPyr-SAM in 0.2 M KOH solution by scanning from -0.2 to -1.2 V (versus Ag|AgCl). Curves (i) and (ii) represent the voltammograms for the bare and SAM-modified gold electrodes, respectively. Two mercaptopyridine desorption peaks were observed at -0.66 and -1.03 V versus Ag|AgCl (Fig. 3a). The appearance of two peaks in this work for the MPyr-SAM is consistent with literature report [34]. As evident from Fig. 3b, coordination with FePc molecule resulted in a shift of the major peak potential at -0.66 to -0.78 V (versus Ag|AgCl), accompanied with a decrease in current density and dramatic disappearance of the minor peak at -1.03 V (versus Ag|AgCl). A shift to a more negative value for the reductive potential desorption is indicative of a monolayer more effectively chemisorbed [34,35], therefore, this result suggests that the FePc-linked-MPyr-SAM is effectively chemisorbed onto the gold electrode, hence proving the coordination of FePc with the pre-formed MPyr-SAM on the gold surface.

3.2. Electrocatalytic oxidation of hydrazine

All the electrocatalytic measurements for hydrazine were performed in pH 7 conditions because of the advantages of neutral pH as stated in Section 1. Importantly, the FePc-SAM-modified electrode exhibited higher catalytic current (at relatively lower potential, $E_p \leq 0.35$ V versus Ag|AgCl) at $\text{pH} \geq 7$ than for $\text{pH} < 7$ for the anodic oxidation of hydrazine. High catalytic activity at $\text{pH} \geq 7$ was also observed by Perez et al. [15] for nickel tetrasulfophthalocyanine com-

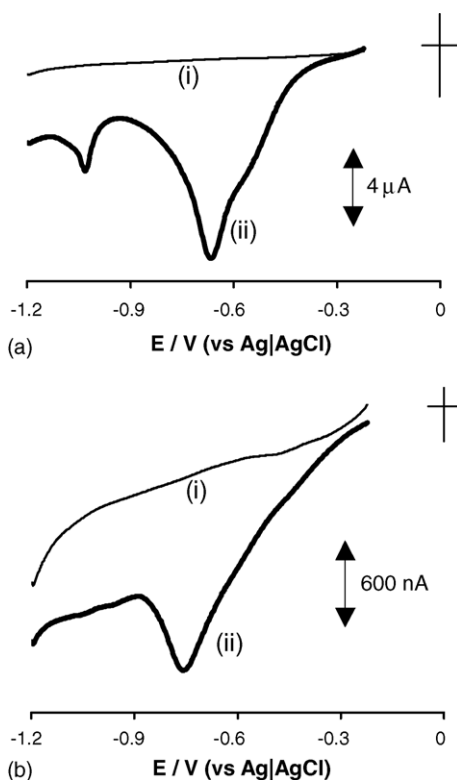


Fig. 3. Cyclic voltammograms for the reductive desorption of (a) MPyr-SAM-modified gold electrode, and (b) FePc-linked-MPyr-SAM-modified gold electrode. Curves (i) and (ii) represent the voltammograms for the bare and SAM-modified gold electrodes, respectively. Electrolyte = 0.2 M KOH solution; scan rate = 50 mV s⁻¹.

plex, which was attributed to the deprotonation of hydrazine providing an easier interaction with the nickel center. Similarly, we may ascribe our observation to the facile axial coordination of the deprotonated hydrazine with the iron center of the FePc-SAM. Each hydrazine solution was de-aerated prior to experiment since it is known [36] that oxygen can react with hydrazine in the presence of transition metal ion to generate hydrogen peroxide and nitrogen. We did not notice any release of gaseous product during the experiment, possibly due to the small concentrations of hydrazine being analysed and/or too low overpotential for bubble formation. Fig. 4 shows the cyclic voltammograms obtained on (a) bare gold electrode, (b) 4-MPyr-SAM-modified gold electrode, and (c) FePc-linked-MPyr-SAM-modified gold electrode in pH 7.0 phosphate buffer solution in the absence (i) and presence (ii) of 9.2×10^{-5} mol/L hydrazine. It is evident that bare gold electrode did not show any detectable oxidation peak due to hydrazine. The same gold electrode modified with the MPyr-SAM showed a broad anodic peak around 0.55 V, typical of a weak electron-transfer process. However, the FePc-linked-MPyr-SAM modified gold electrode exhibited well-defined oxidation peak at 0.35 V (versus Ag/AgCl). The results indicate that MPyr and FePc-MPyr SAMs can be used to enhance electronic communication between the gold electrode and hydrazine. Comparison of the SAMs of MPyr (Fig. 4b) and

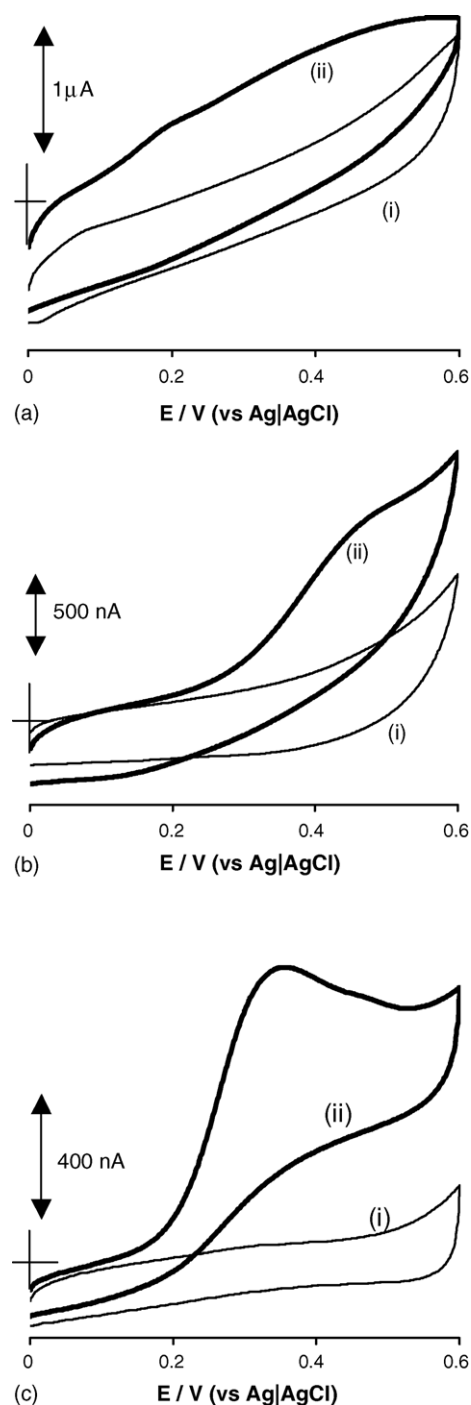


Fig. 4. Comparative cyclic voltammetric responses of (a) bare gold electrode, (b) MPyr-SAM modified gold electrode, and (c) FePc-linked-MPyr-SAM-modified gold electrodes in a pH 7.0 phosphate buffer solution without (i) and with (ii) 9.2×10^{-5} mol/L hydrazine; scan rate = 25 mV s⁻¹.

FePc-MPyr (Fig. 4c) clearly confirms the electrocatalytic activity of the adsorbed FePc towards hydrazine in terms of negative shift of the peak potential (~ 200 mV) and an increase of the current density ($\sim 20\%$). Although, de Sousa et al. [35] and Sawaguchi et al. [37] have earlier reported that gold electrode modified with MPyr-SAM promoted fast electron transfer reaction between gold and cytochrome *c*, it is noteworthy

that our study is the first time it is being observed for hydrazine. The authors [35] suggested the interaction to be due to the binding of the positively charged cytochrome *c* with the weakly basic or anionic functional group of the MPyr-SAM promoter. In our case, it may possibly be due to electrostatic repulsion between the deprotonated hydrazine species and the anionic nitrogen of the MPyr-SAM. However, further experiments are necessary to fully understand this behaviour and its possible analytical applications; all these will form part of our future investigations. It is interesting to compare the CVs reported in the literature for similar anodic oxidations of hydrazine in neutral pH conditions with electrode based on iron(II)tetrasulfophthalocyanine (FeTSPc) supported on titanium oxide coated silica–gel surface [17] and platinum ultramicroelectrode modified with zeolite-containing FePc [18] where the hydrazine oxidation were observed at ~ 0.80 and 0.50 V versus SCE, respectively. Thus, a substantial decrease in overpotential has been achieved in the present study with FePc-linked-MPyr-SAM-modified gold electrode.

Cyclic voltammetry experiments on the influence of different scan rates ($10\text{--}800$ mV s^{-1}) at constant hydrazine concentration (9.2×10^{-5} mol/L) revealed three important information: first, anodic peak current (I_{pa}) is directly proportional to square root of the scan rate ($\nu^{1/2}$) (Fig. 5a) which is an indication of a diffusion-controlled reaction. Second, a plot of $I_{pa}/\nu^{1/2}$ versus ν (Fig. 5b) resulted in the characteristic shape that is typical for a catalytic process. Finally, from the usual equation (Eq. (3)) for a totally irreversible, diffusion-controlled process such as hydrazine oxidation [38,39];

$$E_p = \frac{b}{2} \log \nu + \text{constant} \quad (3)$$

the plot of E_p versus $1/2 \log \nu$ (Fig. 5c) gave a linear relationship, with a Tafel slope ($b = 0.059/an$) of approximately 130 mV/decade, which indicates that the rate-determining step for the electrocatalysis is a one-electron transfer process assuming a transfer coefficient of $\alpha \approx 0.5$ at 298 K. Our results are comparable to literature reports [38,39] using modified electrodes. Salimi and Abdi [39] proposed the involvement of the $\text{Fe}^{(\text{III})}/\text{Fe}^{(\text{II})}$ redox processes for the electrocatalytic oxidation of hydrazine (~ 0.55 V versus Ag|AgCl (3 M KCl)) with cyanoferrate-based carbon composite electrodes at pH 7.0 buffer solution. Based on this report [39] and the formal potential ($E_{1/2} = \sim -0.04$ V versus Ag|AgCl) value of the $\text{Fe}^{(\text{III})}\text{Pc}/\text{Fe}^{(\text{II})}\text{Pc}$ redox processes of the FePc-linked-MPyr-SAM investigated in this work, the basic mechanism through which electrocatalytic oxidation of hydrazine operates at the FePc-MPyr-linked-SAM-modified gold electrode may be represented by Fig. 6. That is, initial oxidation of the $\text{Fe}^{(\text{II})}$ to $\text{Fe}^{(\text{III})}$ followed by the oxidation of hydrazine to its products via $\text{Fe}^{(\text{III})}$ and subsequent regeneration of the $\text{Fe}^{(\text{II})}$ species. The mechanism (Fig. 6) is informative since, until now, it is generally proposed [6,8,16,19] that the oxidation of hydrazine with MPc-based electrodes mostly involve the $\text{M}^{(\text{II})}/\text{M}^{(\text{I})}$ rather than the $\text{M}^{(\text{III})}/\text{M}^{(\text{II})}$ redox couple.

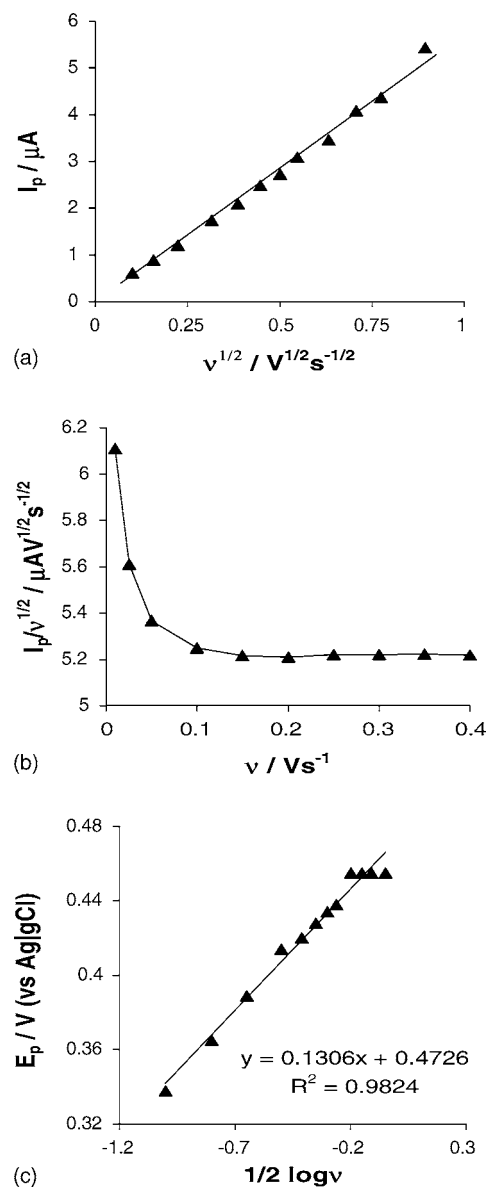


Fig. 5. Plots of (a) I_p vs. $\nu^{1/2}$, (b) $I_p/\nu^{1/2}$ vs. ν , and (c) E_p vs. $1/2 \log \nu$.

3.3. Voltammetric detection of hydrazine

Electrocatalytic detection of hydrazine was investigated with cyclic and Osteryoung square wave voltammetric techniques. Additions of different concentrations of hydrazine solutions resulted in well-defined voltammetric responses at peak potential of 0.35 V versus Ag|AgCl for OSWV (Fig. 7a) and CV (not shown). The plot of peak currents varied linearly with concentrations of the hydrazine over the concentration range of 1.3×10^{-5} to 9.2×10^{-5} mol/L, deviating from linearity at concentrations higher than 1.2×10^{-4} mol/L with a shift to 0.40 V with increasing concentrations (versus Ag|AgCl) (Fig. 7b). The deviation of the plot of I_p versus [hydrazine] from linearity at higher concentration coupled to a shift to more positive potential could be associated to kinetic limitations due to the saturation of hydrazine and its oxidation

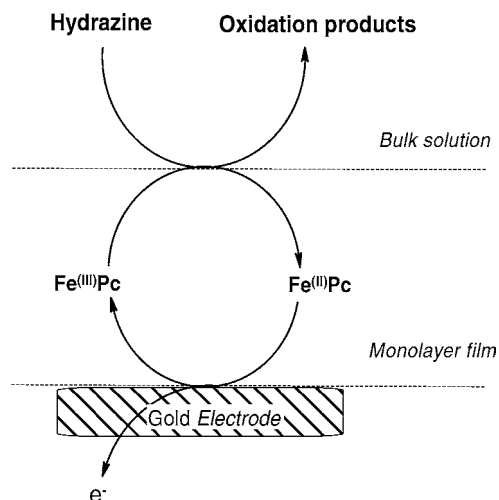


Fig. 6. Schematic representation of anodic oxidation of hydrazine at FePc-linked-MPyr-SAM-modified gold electrode.

products onto the redox-active monolayer film. The limits of detection (ca. 5 and 11 μM for OSWV and CV, respectively) were estimated using the signal-to-noise ratio = 3 criterion and, as expected, OSWV gave a slightly lower detection limit and higher sensitivity ($1.62 \times 10^{-2} \mu\text{A}/\mu\text{M}$ compared to the $9.40 \times 10^{-3} \mu\text{A}/\mu\text{M}$ for CV) than the CV technique. There are no reports on FePc-based electrode for the analysis of hydrazine in neutral or physiological pH conditions with which to compare our present analytical results. However, our detection limit, for example, is in the range reported for CoPc-based electrodes using the more sensitive amper-

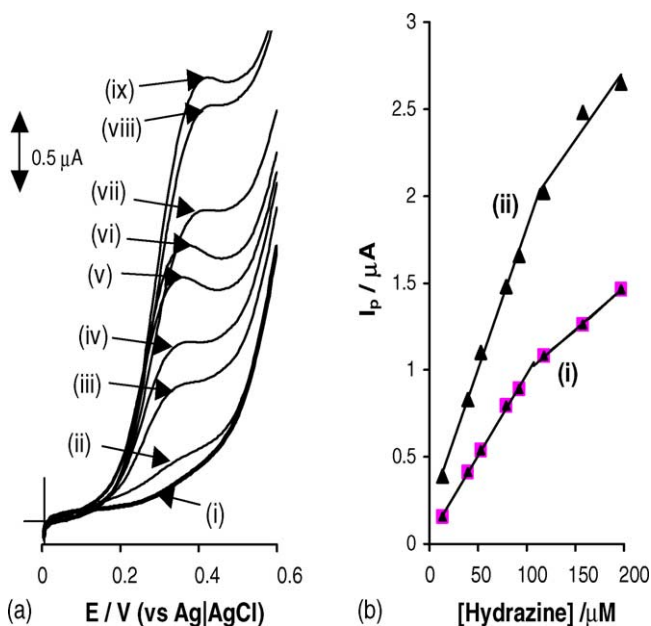


Fig. 7. (a) Osteryoung square wave voltammograms for the increasing additions of (i) 13.2 μM , (ii) 39.5 μM , (iii) 52.6 μM , (iv) 79.0 μM , (v) 92.1 μM , (vi) 118 μM , (vii) 158 μM and (viii) 197 μM hydrazine, and (b) plots of peak currents against hydrazine concentrations obtained at an FePc-linked-MPyr-SAM-modified gold electrode from (i) CV and (ii) OSWV data.

ometric technique [11,13] than the CV and OSWV used in this work. Hence, it can be concluded that the FePc-SAM electrode exhibits very good sensitivity.

An OSWV experiment was performed with fresh tap water sample spiked with hydrazine sulfate with a view to assessing the potential analytical application of the proposed electrode. Ten replicate determinations showed recovery of $99.95 \pm 0.06\%$ of the spike, thus demonstrating the suitability of the proposed FePc-SAM electrode to real sample analysis.

3.4. Electrode stability and repeatability

The cyclic voltammograms did not show any detectable change in shape after 100 scans in aqueous solutions (pH 4 or 7 solutions) at potentials between -0.5 and $+0.9$ V (versus Ag|AgCl), which indicates electrochemical stability. The variation of catalytic peak currents with scan number (20 scans) was investigated at a fixed concentration of hydrazine at 25 mV s^{-1} . A dramatic decrease in peak currents ($>50\%$) was observed after the first scan, which is a typical behaviour for a poisoned electrode. However, on rinsing the electrode in a fresh pH 4 aqueous solution, the electrode surface was renewed and the initial catalytic current was obtained, indicating the reusability of the electrode after analysis. The electrode can be repeatedly used for the analysis of hydrazine for up to a week without significant change in its response. This is a great advantage of the MPc-SAM based electrodes when compared to the other MPc-based electrodes fabricated using, for example, the conventional composite or drop-dry methods.

4. Conclusion

We have described a simple and promising electrode material, based on FePc-linked-mercaptopyridine-self-assembled monolayer film, for direct anodic oxidation and detection of hydrazine in neutral medium. Unlike the widely studied cathodic oxidation of hydrazine with MPc-based electrodes in strong alkaline conditions that involved the $\text{M}^{\text{II}}\text{Pc}/\text{M}^{\text{I}}\text{Pc}$ redox process, the anodic oxidation of hydrazine reported in this work at neutral pH conditions involve $\text{Fe}^{\text{III}}\text{Pc}/\text{Fe}^{\text{II}}\text{Pc}$ redox process. The results described here strongly indicate that FePc-SAM based electrode may be conveniently used in real sample analysis, such as tap water or industrial water at pH 7 conditions. This type of electrode offers certain advantages over conventional electrodes in its ease of fabrication, excellent catalytic activity, sensitivity and simplicity. Thus, FePc-SAM electrodes holds great promises for numerous sensing applications, such as in amperometric sensors for flow-injection analysis.

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