

Sensitive voltammetric determination of 2-mercaptobenzimidazole at electropolymerized nickel and copper tetraaminophthalocyanine membrane modified electrode

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Abstract The voltammetric determination of 2-mercaptobenzimidazole (MBI) was studied by using a glassy carbon electrode (GCE) coated with polymeric nickel and copper tetraaminophthalocyanine (poly-NiTAPc and poly-CuTAPc) membrane. The polymeric membrane decreases the overpotential of oxidation of MBI by 136.2 and 115.0 mV and increases the oxidation peak current by about 3.4 and 3.3 times, while the reduction peak potential shifts positively by 113.0 and 84.1 mV and the peak current increases by about 10 and 7 times in 0.1 mol·l⁻¹ phosphate buffer solution (PBS) at pH=2.0 for poly-NiTAPc and poly-CuTAPc, respectively, compared to the unmodified GCE. The results indicated that the developed electrode exhibited efficient electrocatalytic activity for MBI with relatively high sensitivity, stability, and long life. The oxidation and reduction peak currents of MBI were linear to its concentrations ranging from 8.0×10⁻⁵ to 1.0×10⁻³ mol·l⁻¹ at poly-NiTAPc and from 2.0×10⁻⁵ to 1.0×10⁻³ mol·l⁻¹ at poly-NiTAPc membranes modified electrodes, respectively, with a low limit of detection.

Keywords Electrocatalysis · 2-Mercaptobenzimidazole · Nickel tetraaminophthalocyanine · Copper tetraaminophthalocyanine · Cyclic voltammetry

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Introduction

The development of chemically modified electrodes (CMEs) continues to be an area of great interest due to their numerous applications in electrocatalysis [1–3]. One of the most important properties of CMEs is their ability to catalyze the oxidation or reduction of solute species that exhibits high over voltages at unmodified surfaces. Transition-metal tetraaminophthalocyanine (MTAPc) polymer membranes modified electrodes have been widely studied in the light of increasing stability and electrocatalytic activity of these systems [4]. The electrocatalyses of dopamine [5], NO₂⁻ [6], acetaminophen [7], and thiols [8] have been reported based on polymeric nickel or copper tetraaminophthalocyanine (poly-NiTAPc or poly-CuTAPc). However, to our knowledge, it has not been used for the electrocatalytic study on 2-mercaptobenzimidazole (MBI).

MBI had been widely used as antioxidant for rubbers and plastics, corrosion inhibitor [9, 10], removal of Hg (II) from aqueous media [11], and so on. But it was reported that MBI had potent antithyroid toxicity in rats on 28-day repeated oral dosing [12]. The antithyroid effect of MBI in rats was demonstrated to be more potent than those of thiourea and ethylenethiourea, both well-known antithyroid agents and thyroid carcinogens [13]. Human exposure to MBI occurs because of the use of rubber products processed with this antioxidant and vulcanization accelerator. Airaudo et al. [14] revealed some anesthetic drugs to be contaminated with MBI in the 2.8- to 11.8-ppm range with rubber plunger seals of syringes and/or drug packing containers as the contamination sources. Recently, this rubber antioxidant was also detected in commercial farming rubber boots at levels of 11.5 to 67.7 ppm, this being another possible source of human exposure [15]. MBI is rather stable and might act as an environmental endocrine disrupter.

So the determination of this compound in humans and in the environment is essential for the characterization of its concentration. Many methods for the determination of MBI are developed such as HPLC [16], spectrometric methods [17], and so on. But these methods possess one or more disadvantages of inadequate sensitivity, poor selectivity, time-consuming, and low analytic recovery. In addition, unsubstituted cobalt phthalocyanine (CoPc) carbon paste electrode were also used for the potentiometric detection of MBI [18], the carbon paste electrode allowed sensors to be created with either renewable or disposable surfaces, low cost, simple preparation, and low background current. Despite the mentioned advantages, the carbon paste electrode exhibited severe limitations listed as follows: (1) weak mechanical properties due to their creamy texture, which can easily lead to the disintegration of the system; (2) poor reproducibility of the electrode fabrication; (3) leakage of mediator out of the carbon paste. But the poly-NiTAPc and poly-CuTAPc membrane can yield uniform, electroconducting, robust, and strongly adherent coating and ensure reproducible control over the thickness compared to the carbon paste electrode.

This work was concerned with the development of an amperometric method for the determination of MBI at a glassy carbon electrode (GCE) modified with poly-NiTAPc and poly-CuTAPc membranes as an electrocatalyst. The results showed that these poly-NiTAPc and poly-CuTAPc membranes act not only as real catalysts toward the oxidation of MBI but also act as a catalyst toward the reduction of the corresponding disulfide in acidic solution (pH=2).

Experimental

Materials

NiTAPc and CuTAPc were synthesized according to literature methods [19] and their structures are shown in Fig. 1.

Tetrabutylammonium perchlorate (TBAP) was synthesized by following method. Tetrabutylammonium bromide (32.0 g) was dissolved in 200.0 ml water. To the solution, 16.0 ml perchloric acid was added slowly under stirring; the resulting mixture was cooled to room temperature and filtered. The white solid product obtained was washed with water until no bromide was detected, then dried in a vacuum desiccator.

MBI ($\geq 98\%$) was commercially purchased (Acros Organics, Springfield, NJ, USA) and used without further purification. All other chemicals were of analytical reagent grade.

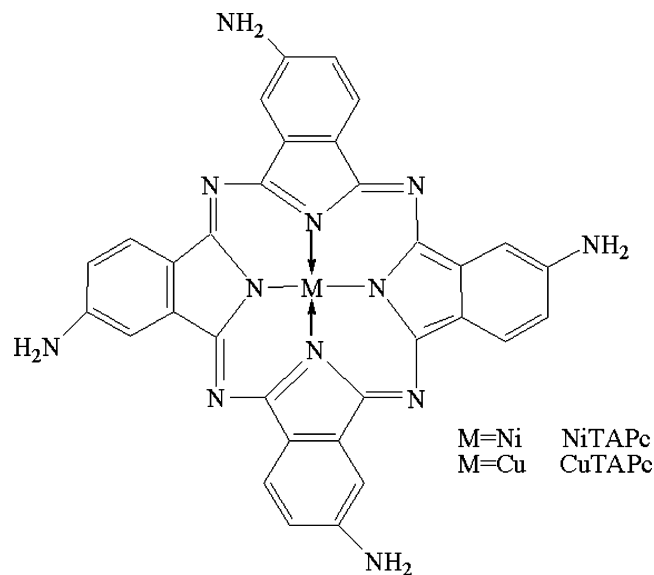


Fig. 1 Structural formulas of NiTAPc and CuTAPc

Apparatus

Electrochemical measurements were performed on a CHI 400 electrochemical system (Shanghai ChengHua Instrument, Shanghai, China). A three-electrode system was used, including a bare GCE ($\Phi=3.0$ mm) or modified electrode as working electrode, a Ag/AgCl (saturated KCl) electrode as the reference electrode, and a platinum wire electrode as counter electrode.

Membrane preparation

Before the polymerization, the GCE was polished to a mirror-like surface with $0.05 \mu\text{m}$ Al_2O_3 slurry, then rinsed and ultrasonicated thoroughly in 50% nitric acid, ethanol, and distilled water subsequently. The polymeric membranes were grown by voltammetric repetitive cycling at the GCE between -0.4000 and $+1.0000$ V at $100 \text{ mV}\cdot\text{s}^{-1}$ in a dimethyl formamide (DMF) solution containing $5.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ NiTAPc or CuTAPc monomer and $0.10 \text{ mol}\cdot\text{l}^{-1}$ TBAP. The modified electrode was rinsed with DMF, ethanol, and then with distilled water before voltammetric measurements.

Preparation of MBI and sample solution

Stock solutions of MBI was made up daily and brought to the desired concentration and pH by dilution just before use. Cyclic voltammetric (CV) experiments were carried out in a background electrolyte of $0.1 \text{ mol}\cdot\text{l}^{-1}$ phosphate buffer solution (PBS).

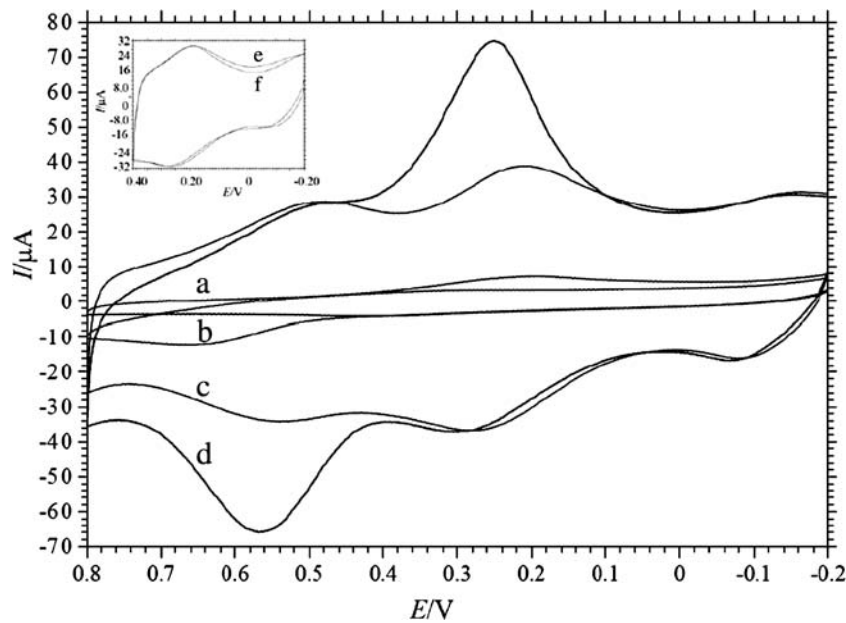


Fig. 2 Cyclic voltammograms of unmodified GCE (a and b) and poly-NiTAPc (c and d) modified electrode in the presence of $0 \text{ mol}\cdot\text{l}^{-1}$ (a and c) and $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI (b and d) in $\text{pH}=2.0$ PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$. Inset shows the cyclic voltammograms of poly-

NiTAPc modified electrode in the presence of $0 \text{ mol}\cdot\text{l}^{-1}$ (e) and $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI (f) when the upper limit of the positive scan is limited to 0.4000 V in $\text{pH}=2.0$ PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$

The serum urine samples, obtained from healthy volunteers, were spiked with MBI at different concentrations. The mixtures were vortexed for 1–2 min and centrifuged at 12,000 rpm for 10 min at $4 \text{ }^\circ\text{C}$; afterward, an aliquot of the upper phase solution was brought to the desired concentration and pH by dilution with $0.1 \text{ mol}\cdot\text{l}^{-1}$ PBS just before the voltammetric determination.

Results and discussion

Electrochemical behavior of MBI

Figures 2 and 3 show the cyclic voltammograms of MBI at unmodified GCE and at the poly-NiTAPc and poly-CuTAPc modified electrode, respectively, at $\text{pH}=2.0$ PBS

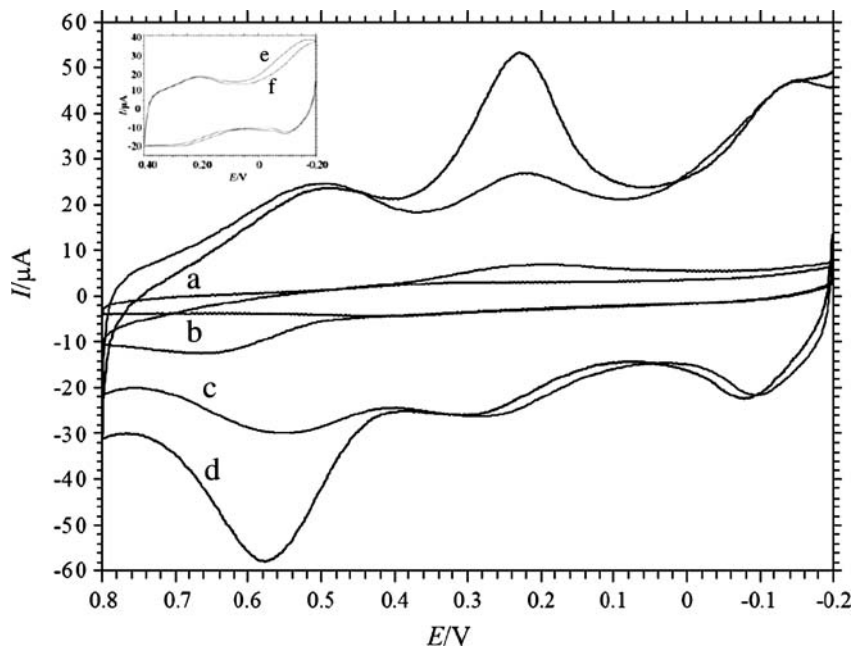


Fig. 3 Cyclic voltammograms of unmodified GCE (a and b) and poly-CuTAPc (c and d) modified electrode in the presence of $0 \text{ mol}\cdot\text{l}^{-1}$ (a and c) and $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI (b and d) in $\text{pH}=2.0$ PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$. Inset shows the cyclic voltammograms of poly-

CuTAPc modified electrode in the presence of $0 \text{ mol}\cdot\text{l}^{-1}$ (e) and $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI (f) when the upper limit of the positive scan is limited to 0.4000 V in $\text{pH}=2.0$ PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$

in the absence and presence of $1.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ MBI. The electrochemical response of MBI at an unmodified GCE under such conditions is rather poor with broad peak shape. The oxidation peak of MBI exhibited at approximately +0.6931 V with the peak current of about 8.693 μA . Similarly, there is no significant reduction peak, and the estimate of the peak current value is 3.875 μA at approximately 0.1438 V. However, the sensitivity and selectivity of the electrochemical analysis can be enhanced using the poly-NiTAPc or poly-CuTAPc modified electrode. In the potential range from -0.2000 to 0.8000 V, the cyclic voltammogram of a poly-NiTAPc electrode recorded in the absence of MBI in a pH=2.0 PBS showed three redox peaks, the well-defined pair of peak located at approximately $E_{\text{eq}}=0.5103 \text{ V}$, $E_{\text{eq}}=(E_{\text{pa}}+E_{\text{pc}})/2$ where E_{pa} and E_{pc} are the potential values of the anodic and the cathodic voltammetric peaks for the redox process, can be assigned, as reported in the literature for other nickel phthalocyanine [6, 20–22] to the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox processes. Under the condition mentioned above, the cyclic voltammogram of a poly-CuTAPc electrode shows three redox peaks, the well-defined pair of peak located at approximately $E_{\text{eq}}=0.5247 \text{ V}$ can be assigned to the $\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$ redox processes, as reported in the literature for other copper phthalocyanine [8] and similar to those reported above for nickel phthalocyanine.

With the addition of MBI in the buffer solution, at the poly-NiTAPc modified electrode, the appearance of the oxidation peak at 0.5569 V with 29.630 μA peak current is concomitant with that of a reduction peak at 0.2568 V with 35.650 μA peak current during the reverse scan, which are located close to the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox process. Under the same condition, similarly, the sensitive oxidation peak for MBI at the poly-CuTAPc modified electrode was observed at 0.5781 V with 28.630 μA peak current and is concomitant with a sensitive cathodic peak appeared clearly at 0.2279 V with 26.390 μA peak current, which are located close to the $\text{Cu}^{\text{III}}/\text{Cu}^{\text{II}}$ redox process.

According to previously reported studies on the electrocatalytic oxidation of thiols by adsorbed and polymer-based metallophthalocyanines [20, 23–33], the large oxidation current observed was related to the electrocatalytic oxidation of MBI, the large cathodic peak might be related to the reduction of the corresponding disulfide. Indeed, if the upper limit of the positive scan is limited to a smaller potential than the $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ redox processes ($\text{M}=\text{Ni}$ or Cu) and at the same working conditions, the large oxidation and cathodic peaks do not appear shown in the inset in Figs. 2 and 3, similar to the one observed without MBI. So, the large cathodic peak could be due to the reduction of a product generated during the MBI oxidation and the reduction current linked to the disulfide reduction. These results mentioned above clearly showed that the poly-NiTAPc and poly-CuTAPc membranes acted not only as

real catalysts toward the oxidation of MBI but also acted as catalyst toward the reduction of the corresponding disulfide because they decreased the overpotentials of the redox processes and greatly enhanced the peak currents compared with those obtained at nonmodified electrodes. The potential at which a catalytic current was observed in this experiment was closely related to the $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ couple in the polymer which facilitates the electron transfer between the electrode and the analyte; this showed that MTAPc was functioning as a redox mediator for MBI electrooxidation. It was assumed that the catalytic behaviors of the poly-NiTAPc and poly-CuTAPc membranes were associated with the redox activity of the central metal. In the light of the obtained results and the mechanism proposed in literature [20, 21, 28, 30, 32, 34–40], therefore, we could suggest the following mechanism for the electrocatalytic oxidation of MBI:



where RSH is MBI and RSSR is the corresponding disulfide.

In acidic medium, in step 1, some adduct produced is formed by the coordination axially between M(II)TAPc and MBI at free axial positions of the planar metal complex before the electrochemical reaction. Then the electrochemical oxidation of the M(II) compound to an M(III) species in step 2 is probably rapid. This is followed by a slow chemical step 3 involving the rupture of the M-S bond in the adduct, which also serves to generate the M(II) form of MTAPC. The thyl radical then reacts very rapidly in step 4 to form the disulfide.

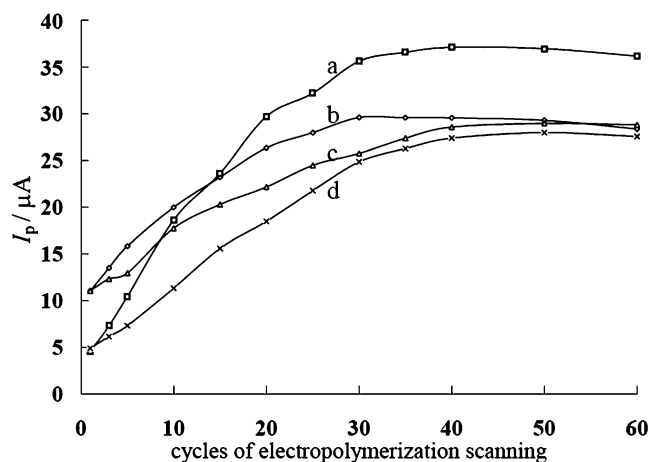
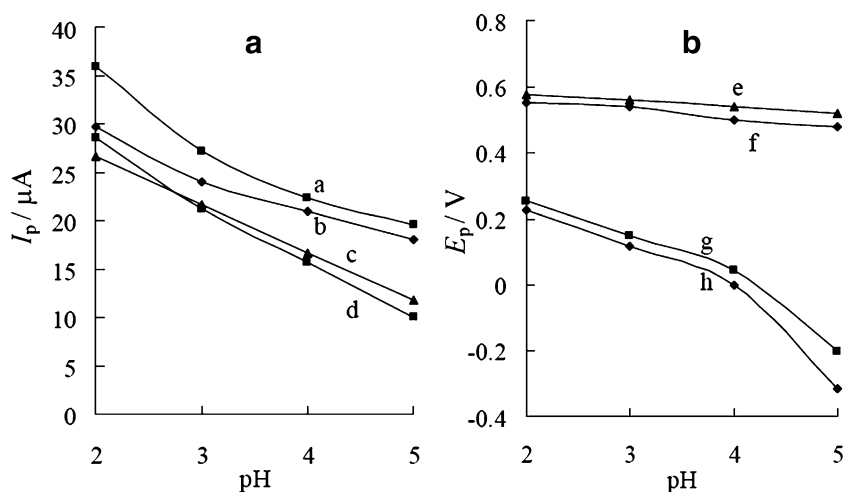


Fig. 4 Effect of membrane thickness (cycles of electropolymerization scanning) on the catalytic oxidation (**b** and **c**) and reduction (**a** and **d**) peak currents of $1.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ MBI at the poly-NiTAPc (**a** and **b**) and poly-CuTAPc (**c** and **d**) modified electrode in pH=2.0 PBS; scan rate=60 $\text{mV} \cdot \text{s}^{-1}$

Fig. 5 Effect of pH on the catalytic peak current (a) and potential (b) of $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI at the poly-NiTAPc (a $I_{p_c}/\mu\text{A}$, b $I_{p_a}/\mu\text{A}$, f E_{p_a}/V , g E_{p_c}/V) and poly-CuTAPc (c $I_{p_c}/\mu\text{A}$, d $I_{p_a}/\mu\text{A}$, e E_{p_a}/V , h E_{p_c}/V) modified electrode in $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI; scan rate = $60 \text{ mV}\cdot\text{s}^{-1}$



Effect of the thickness of the polymeric membrane

Repetitive cycling around the MTAPc ligand oxidation results in the polymerization of the complex and the deposition of an electroactive polymeric membrane on the electrode surface and the responses of the poly-NiTAPc and poly-CuTAPc modified electrode were dependent on the thickness of the membrane. Absolute data on the thickness were not measured; however, the thickness was known to be controlled most simply by varying the cycles of electropolymerization scanning. The membrane thickness was supposed to be proportional to the scanning cycles of the polymerization [41–43]. Figure 4 illuminates the effect of membranes thickness on the catalytic peak currents for $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI in pH=2.0 PBS. The results indicated that the catalytic activity rose with the thickness of the polymer membrane increasing due to the increasing of the catalytic active centers. In addition, the experiments found that the membranes were unstable when cycles of electropolymerization scanning were very small. On the other hand, when the membranes were too thick, the catalytic activity decreased because the membranes would

hinder the transfer of electron. Consequently, 30 and 40 cycles of electropolymerization scanning provided the optimum polymeric membrane thickness for the poly-NiTAPc and poly-CuTAPc modified electrode, respectively, and a layer of greenish blue membrane was obtained.

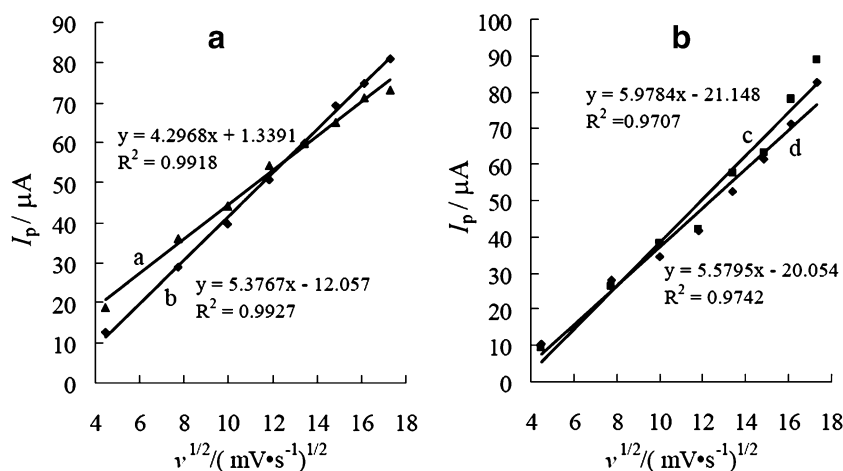
Effect of pH on catalytic behavior

Figure 5 showed that the oxidation and reduction peak potentials shifted negatively, and the oxidation and reduction currents decreased with the increase of pH in the range of pH studied; it meant that the catalytic activity of poly-MTAPc membrane decreased with the increase of pH. When pH was higher than 5, both peaks became poorly defined. Bearing this in mind, a pH value of 2.0 was selected for subsequent work, as it was the optimum for improving MBI stability and current response.

Effect of scan rate on oxidation current

With the increase in scan rate, the peak current increased and the peak potential shifted positively. The plots of the

Fig. 6 Effect of scan rate on catalytic oxidation (b and d) and reduction (a and c) peak current of $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI at a poly-NiTAPc (a) and poly-CuTAPc (b) modified electrode in pH=2.0 PBS



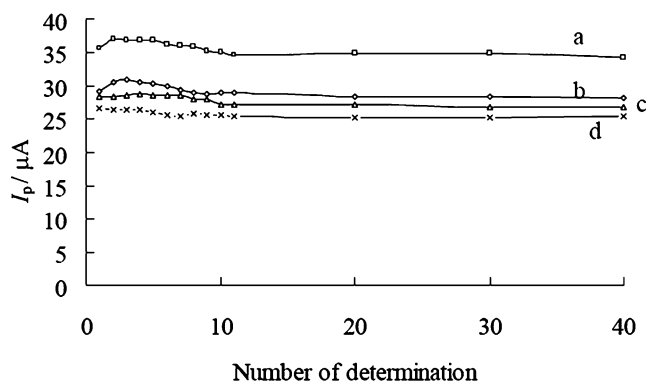


Fig. 7 The catalytic oxidation (b and c) and reduction (a and d) peak current of $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI on the number of determinations at the poly-NiTAPc (a and b) and poly-CuTAPc (c and d) modified electrode in pH=2.0 PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$

oxidation and reduction peaks peak current (I_p) vs $v^{1/2}$ were constructed in a pH=2.0 PBS in the presence of $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI. The intensities of the oxidation and reduction peaks related to the thiol redox processes vary linearly with the square root of the potential scan rate in the scan rate range of 20–300 $\text{mV}\cdot\text{s}^{-1}$ (Fig. 6), which indicated that the oxidation of MBI and reduction of the corresponding oxidation product at the poly-MTAPc membrane electrode was diffusion-controlled in the scan rate range of 20–300 $\text{mV}\cdot\text{s}^{-1}$ [42]. When scan rate was higher than 300 $\text{mV}\cdot\text{s}^{-1}$, both peaks became poorly defined.

Stability of the membrane

To ensure that the method was performed appropriately, the system stability was required before routine use. To determine the stability of the poly-NiTAPc and poly-CuTAPc membranes, the oxidation and reduction peak current responses to $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ MBI were recorded 40 times within a day (Fig. 7); the near horizontal line of the graph indicated that the poly-NiTAPc and poly-CuTAPc

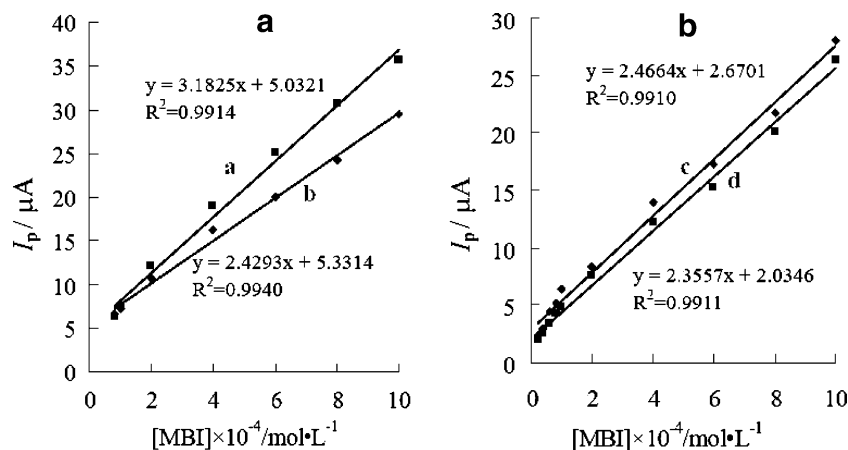
membrane modified electrode was durable (giving 40 determinations without significant loss of response), and our system was stable for long-time routine analysis. Moreover, the modified electrode could retain above 80% of its original response after 30 days of storage. The relatively high stability of membranes showed it was fit for routine use.

Linearity and detection limits for MBI

The oxidation and reduction peak current were chosen as the quantitative criterion. There was a good linear relationship between peak current and concentration. To determine the linear calibration curve, correlation coefficient, and detection limit of MBI at the poly-NiTAPc and poly-CuTAPc electrode, a series of MBI solutions were tested in pH=2.0 PBS at $60 \text{ mV}\cdot\text{s}^{-1}$. The intensity of the oxidation and reduction peak was directly proportional to the concentration of MBI in the concentration range of 8.0×10^{-5} to $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ at poly-NiTAPc (Fig. 8a) and 2.0×10^{-5} to $1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ at poly-NiTAPc (Fig. 8b) membranes modified electrodes, respectively. Moreover, in the presence of MBI, the peak potential MBI oxidation shifted to positive value and enhanced upon increasing the concentration of MBI (not shown). In fact, these observations are indicative of an interaction of MBI with the metal central of MTAPc.

The peak currents for the first repetitive five determinations of $1.0 \times 10^{-5} \text{ mol}\cdot\text{l}^{-1}$ MBI were recorded in pH=2.0 PBS at $60 \text{ mV}\cdot\text{s}^{-1}$, then the theoretical detection limits (D) for MBI could be obtained from the following equation: $D=3sc/I_p$ where c is the concentration of MBI ($\text{mol}\cdot\text{l}^{-1}$), I_p and s are the mean and the SD of the peak currents (μA), respectively. At the poly-NiTAPc membrane modified electrode, the detection limits are estimated to be 4.0×10^{-7} and $2.0 \times 10^{-7} \text{ mol}\cdot\text{l}^{-1}$ with oxidation and reduction current

Fig. 8 Effect of concentration of MBI on catalytic oxidation (b and c) and reduction (a and d) peak current at a poly-NiTAPc (a) and poly-CuTAPc (b) modified electrode in pH=2.0 PBS; scan rate= $60 \text{ mV}\cdot\text{s}^{-1}$



peak as quantitative criterion, respectively. At poly-CuTAPc membrane modified electrode, the detection limits are estimated to be $2.0 \times 10^{-7} \text{ mol}\cdot\text{l}^{-1}$ with both oxidation and reduction current peak as quantitative criterion.

Interferences and application

The effect of some possible interferences commonly found in humans and in the environment were investigated using amperometry. The results showed that the common inorganic ions (such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Cl^- , Br^- , SO_4^{2-} , etc.) 100 times as much as the MBI concentration did not preclude the use of the electrode to analyze MBI. Other organic compounds such as glucose ($1.0 \times 10^{-2} \text{ mol}\cdot\text{l}^{-1}$) and urea ($1.0 \times 10^{-2} \text{ mol}\cdot\text{l}^{-1}$) also did not interfere with the determination. Uric acid ($1.0 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$) that was active near potential of 0.8000 V did not interfere with the detection of MBI. Cysteine and ascorbic acid might slightly interfere if they were present.

The proposed method was applied to the determination of MBI in spiked human urine. The serum urine samples, obtained from healthy volunteers, were spiked with MBI at different concentrations, and treated as described in the “Preparation of MBI and sample solution” section. The concentrations of MBI were calculated from the calibration graph. The results indicated that the satisfactory recoveries obtained with such a simple sample procedure were in the range of 94.3–109.4% (RSD=3.45–5.36%). The proposed method provided a high sensitivity, accuracy, and precision of the results.

Conclusions

The poly-NiTAPc and poly-CuTAPc modified electrodes have been prepared by electropolymerization on the GCE. The modified CMEs are successfully applied as a very sensitive voltammetric sensor for the detection of MBI. The results prove that poly-NiTAPc and poly-CuTAPc membranes can enhance the catalytic rule of the electron mediator, leading to lowering the overpotential and increasing the sharpness and peak current of oxidation of MBI and the reduction of the corresponding disulfide in acidic solution (pH=2). In addition, the modified electrodes showed many profits such as relatively long-term operational stability, high sensitivity, reproducible responses, and a wide linear range of the calibration plot for the determination of MBI. In this sense, the above advantages together with easy preparation make the poly-NiTAPc and poly-CuTAPc modified electrodes useful amperometric sensors of MBI. Further work is necessary to understand the catalytic mechanisms.

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