

# Electrocatalytic Activity of Electropolymerized Cobalt Tetraaminophthalocyanine Film Modified Electrode towards 6-Mercaptopurine and 2-Mercaptobenzimidazole

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## ABSTRACT

The electrocatalytic activity of electropolymerized cobalt tetraaminophthalocyanine (poly-CoTAPc) film modified on the glassy carbon electrode (GCE) towards 6-mercaptopurine (6MP) and 2-Mercaptobenzimidazole (MBI) was studied. Comparing with the case at the unmodified GCE, the poly-CoTAPc film decreased the overpotential of oxidation of 6MP ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) and MBI ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) by 335 and 189 mV, respectively, and increased the peak current by about 3 and 2 times, respectively, while the reduction potential of the disulphide product of previous oxidation of 6MP shifted positively by 312 mV and the peak current increased by 40 times in 0.1 mol L<sup>-1</sup> phosphate buffer solution (PBS, pH = 2.0). The poly-CoTAPc film exhibited efficiently electrocatalytic activity for 6MP and MBI with relatively high sensitivity, stability and long-life.

## KEYWORDS

Electrocatalysis, 6-mercaptopurine, 2-mercaptobenzimidazole, cobalt tetraaminophthalocyanine, electropolymeric film.

## 1. Introduction

6-mercaptopurine (6MP) is a purine antimetabolite used for many years along with other drugs in the treatment of leukemia in children. It is a substantial drug in the remission maintenance chemotherapy in children with acute lymphoblastic leukemia (ALL).<sup>1</sup> However, this drug can not distinguish cancer and normal cells, it causes adverse effects,<sup>1-4</sup> since some normal cells are affected. 2-Mercaptobenzimidazole (MBI) has been widely used for antioxidant for rubbers and plastics, corrosion inhibitor, removal of Hg(II) from aqueous media, and so on. But it had potent antithyroid toxicity in rats on 28-day repeated oral dosing. Human exposure to MBI occurs because of the use of rubber products processed with this antioxidant and vulcanization accelerator.<sup>8,9</sup> MBI is rather stable and might act as an environmental endocrine disrupter.

6MP and MBI belong to thiols (RSH), as above all, the determination of these sulphhydryl compounds in human metabolism is essential for the characterization of their concentrations, physiological activities or controlling administrations. Various methods for the determination of 6MP have been developed in literatures such as high-performance liquid chromatography (HPLC)<sup>10</sup> and capillary electrophoresis<sup>11</sup> with UV absorbance detection. In order to obtain an effective separation and sensitive detection, HPLC coupled to electrochemical detector<sup>2-15</sup> has been used. Spectrofluorometry method<sup>16-19</sup> also has been used to determine 6MP. Various methods for the determination of MBI have also been developed such as HPLC coupled to tandem mass spectrometry,<sup>20-21</sup> gas chromatography/mass spectrometry<sup>22</sup> and spectrometric methods.<sup>23</sup> The electrochemical reaction or adsorption of 6MP or MBI on some electrodes such as Hg,<sup>24-26</sup> Au,<sup>24,27-29</sup> Ag,<sup>30-32</sup> Cu,<sup>33</sup> has extensively been reported. Moreover, voltammetric methods have shown the advantages of inexpen-

sive utilization, small-size instrumentation and low operating cost. So, electrochemical methods have attracted a lot of attention for the determination of 6MP<sup>34</sup> or MBI.<sup>35,36</sup>

The preparation and properties of polymer film modified electrodes continue to be an area of great interest because of their numerous applications on electrocatalysis.<sup>37,38</sup> Such modified films can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve the stability. Up to now, different methodologies have been used to prepare polymeric film modified electrodes; among them electropolymerization has demonstrated to be a very convenient means for immobilizing polymers on various conductive substrates, because the deposition can be controlled by adjusting the electrochemical parameters and the process is located on the electrode surfaces. Moreover, the thickness, permeation and charge transport characteristics of the modified polymeric films can be well defined<sup>39,40</sup>. Therefore, electro-polymeric film modified electrodes recently have received extensive interest in the detection of many analytes because of its high selectivity, sensitivity, strong adherence to electrode surface and chemical stability of the films. Transition-metal tetraaminophthalocyanine polymeric film modified electrodes have been widely studied, in light of high stability and electrocatalytic activity of these systems.<sup>41-43</sup> In particular, much interest has been focused on electropolymerized cobalt tetraaminophthalocyanine (poly-CoTAPc) film modified electrode, because of its excellent chemical stability and mechanical durability. The poly-CoTAPc films have been used as electrocatalysts in determination of some thiols;<sup>14,44,45</sup> however, the electrocatalytic behaviour of electropolymerized CoTAPc film towards 6MP or MBI was not studied in detail. Therefore, it was worthwhile to further study the electrocatalytic behaviour of electropolymerized CoTAPc film towards 6MP and MBI.

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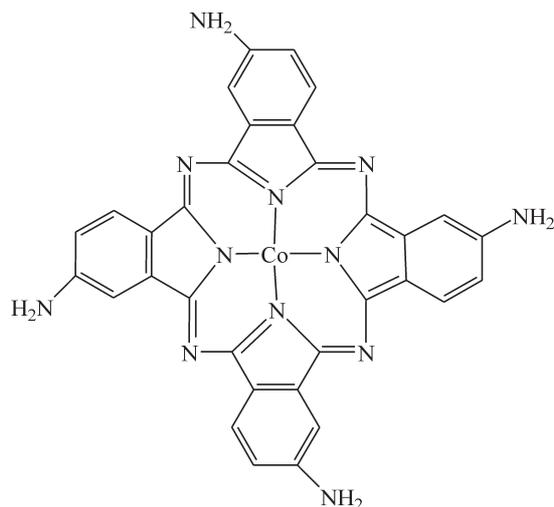


Figure 1 Molecular structure of CoTAPc.

## 2. Experimental

### 2.1. Chemicals and Materials

CoTAPc was synthesized according to the literature methods<sup>46</sup> and its structure is 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.

6MP ( $\geq 98\%$ ) and MBI ( $\geq 98\%$ ) were commercially purchased from Shanghai Chemical Reagent Corporation (Shanghai, China) and Acros Organics (New Jersey, USA), respectively, and they were used without further purification. All other chemicals were of analytical reagent grade.

### 2.2. Apparatus

Electrochemical measurements were performed on a CHI 400 electrochemical system (Shanghai ChengHua Instrument

Company, 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.

### 2.3. Preparation of Poly-CoTAPc Film Modified GCE

Prior to the polymerization, the GCE was polished to a mirror-like surface with  $0.05 \mu\text{m}$   $\text{Al}_2\text{O}_3$  slurry, then rinsed and ultrasonicated thoroughly in 50.0 % nitric acid, ethanol and distilled water subsequently. The polymeric films were grown by potentiodynamically repetitive cycling at the GCE between  $-0.4$  and  $+1.0$  V at  $100 \text{ mV s}^{-1}$  in a dimethyl formamide (DMF) solution containing  $5.0 \times 10^{-3} \text{ mol L}^{-1}$  CoTAPc monomer and  $0.10 \text{ mol L}^{-1}$  TBAP. The modified electrode was rinsed with DMF, ethanol and then with distilled water prior to voltammetric measurements.

### 2.4. Preparation of 6MP, MBI and Sample Solution

Stock solutions of 6MP or MBI were made up daily, then brought to the desired concentration and pH by dilution just prior to use. Cyclic voltammetric (CV) experiments were carried out in a background electrolyte of  $0.1 \text{ mol L}^{-1}$  PBS.

The urine samples, obtained from healthy volunteers, were spiked with 6MP or MBI at different concentrations. The mixtures were vortexed for 1–2 min and centrifuged at 12 000 rpm for 10 min at  $4^\circ\text{C}$ , afterward, an aliquot of the upper phase solution was brought to desired concentration and pH by dilution with  $0.1 \text{ mol L}^{-1}$  PBS just prior to the voltammetric determinations.

## 3. Results and Discussion

### 3.1. Electrochemical Behaviour of 6MP and MBI

In the potential range from  $-0.2$  to  $0.8$  V, the cyclic voltammogram of a poly-CoTAPc electrode recorded in the absence of 6MP and MBI in a  $\text{pH} = 2.0$  PBS showed two pairs of redox peaks in Figs 2c and 3c, respectively. The well-defined pair of peaks located at approximately  $E_{\text{eq}} = 0.432$  V ( $E_{\text{eq}} = (E_{\text{pa}} + E_{\text{pc}})/2$ , where  $E_{\text{pa}}$  and  $E_{\text{pc}}$  were the potential values of the anodic and the

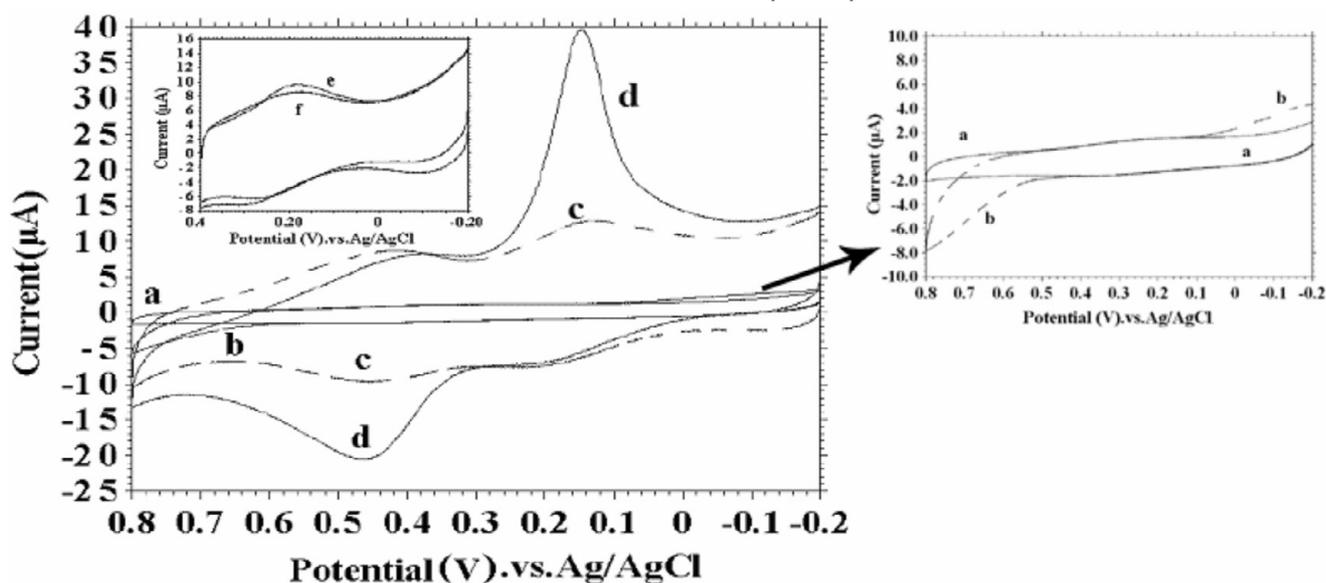
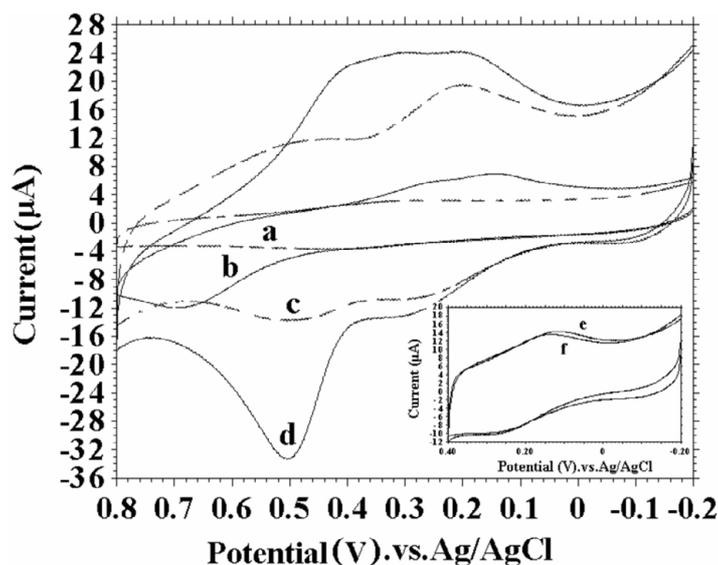


Figure 2 Cyclic voltammograms of unmodified GCE (a and b) and poly-CoTAPc modified electrode (c and d) in the presence of  $0 \text{ mol L}^{-1}$  (a and c) and  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  6MP (b and d) in  $\text{pH} = 2.0$  PBS, scan rate =  $60 \text{ mV s}^{-1}$ . Inset shows cyclic voltammograms of poly-CoTAPc modified electrode in the presence of  $0 \text{ mol L}^{-1}$  (e) and  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  6MP (f) when the upper limit of the positive scan is limited to  $0.4$  V in  $\text{pH} = 2.0$  PBS; scan rate =  $60 \text{ mV s}^{-1}$ .



**Figure 3** Cyclic voltammograms of unmodified GCE (a and b) and poly-CoTAPc (c and d) modified electrode in the presence of MBI (the experimental conditions are as same as those described in Figure 2).

cathodic voltammetric peaks for the redox process, respectively), could be assigned, as reported in the literature,<sup>47–53</sup> to the Co(III)/Co(II) redox processes, whose cathodic and anodic peak potential were 0.413 V and 0.45 V, respectively. A second couple of peaks in the proximity of +0.2 V were also observed, still in the absence of 6MP or MBI, which can be attributed to the Co(II)/Co(I) redox processes according to the literature.<sup>47–53</sup>

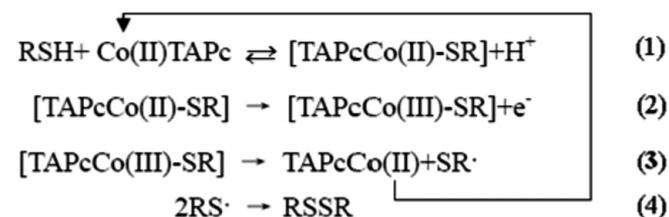
Poly-CoTAPc film has shown great promise for decreasing the overpotential required for the determination of many compounds; hence this redox mediator was evaluated for the detection of 6MP and MBI. Electrochemical properties of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> 6MP and MBI at unmodified GCE (Figs 2b and 3b, respectively) and at the poly-CoTAPc film modified electrode (Figs 2d and 3d, respectively) were recorded in 0.1 mol L<sup>-1</sup> PBS (pH = 2.0). Under such experimental conditions, the direct oxidation of 6MP and MBI at an unmodified GCE showed relatively weak redox waves with a small ill-defined peak. However, the sensitivity and selectivity of electrochemical analysis could be enhanced using the poly-CoTAPc film modified electrode. Under the same conditions, for each compound at the poly-CoTAPc film modified electrode, a huge increase in the catalytic redox current with the foot around the Co(III)/Co(II) redox potential, was observed (Figs 2d and 3d); the appearance of the oxidation peak at 0.46 V and 0.504 V for 6MP and MBI, respectively, which was concomitant with a reduction peak at 0.147 V for 6MP and a poor shape reduction peak with high peak current for MBI during the reverse scan. In brief, the poly-CoTAPc film decreases the overpotential of oxidation of 6MP and MBI by 335 and 189 mV and increases the oxidation current by about 3 and 2 times, respectively. At the same time, the reduction potential of the disulphide product of previous oxidation of 6MP shifted positively by 312.0 mV and the peak current increased by about 40 times compared to the unmodified GCE.

According to previously reported studies on the electrocatalytic oxidation of thiols by adsorbed or polymer-based metallophthalocyanines<sup>14,44–45,54</sup>, we assumed that the large oxidation current observed was related to the electrocatalytic oxidation of 6MP or MBI, the large cathodic peak might be related to the reduction of the corresponding disulphide. Indeed, if the upper limit of the positive scan was limited to a smaller potential than the Co(III)/Co(II) redox processes and at the same working conditions, the large oxidation and cathodic

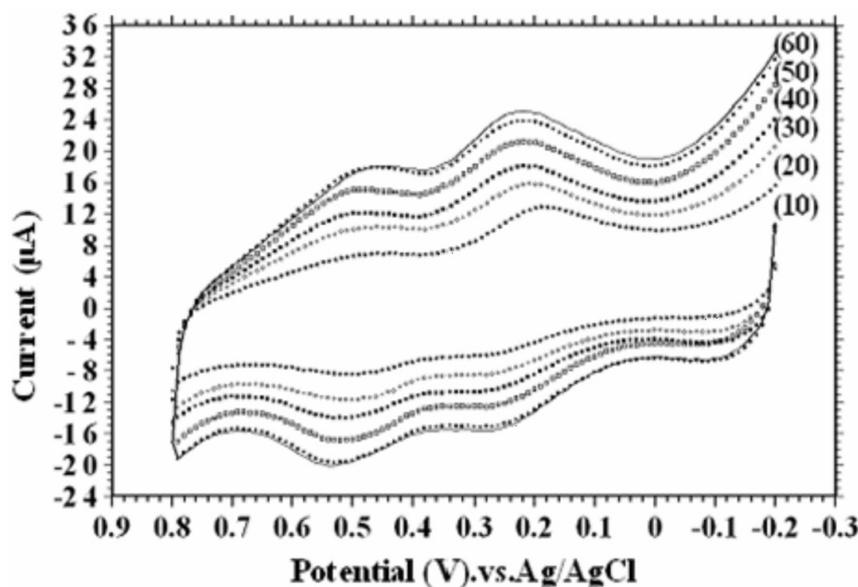
peaks did not appear (shown in the inset in Figs 2 and 3), similar to those observed without 6MP or MBI. So, the large cathodic peak could be due to reduction of a product generated during the 6MP or MBI oxidation and the reduction current linked to the disulphide reduction. It also showed that the oxidation of the 6MP or MBI occurred at potentials where Co(III) species predominated, whereas the reduction of the disulphide occurred after the Co centre was reduced to Co(II) within the poly-CoTAPc film. These results mentioned above clearly showed that the poly-CoTAPc acted not only as a real catalyst towards the oxidation of 6MP and MBI but also acted as a catalyst towards the reduction of the corresponding disulphide, since they decreased the overpotentials of the redox processes and greatly enhanced the peak currents. The potential of the catalytic current was closely related to the Co(III)/Co(II) couple in the polymer film which facilitated the electron transfer between the electrode and the analyte, this also showed that the CoTAPc was functioning as a redox mediator for 6MP or MBI electro-oxidation. Therefore, it was assumed that the catalytic behaviours of poly-CoTAPc film were associated with the redox activity of the central metal.

The mechanisms of the electrocatalytic redox of thiols have been extensively reported in references.<sup>14,36,44–45,54–60</sup> In the light of the results obtained and the mechanism proposed in literature<sup>61–66</sup>, in an acidic solution, the catalytic mechanism should involve the Co(III)/Co(II) redox couple, therefore, the catalysis of poly-CoTAPc film towards 6MP or MBI could be explained by following mechanisms:

As shown in Equation 1 (Scheme 1), in acidic media some adduct product was formed by the coordination axially between Co(II)TAPc and RSH at free axial positions of the planar metal



**Scheme 1**  
Catalytic mechanism of 6MP or MBI redox at poly-CoTAPc modified electrode in acidic media.



**Figure 4** Cyclic voltammograms of poly-CoTAPc modified electrodes in pH = 2.0 PBS, scan rate = 60 mV s<sup>-1</sup>. Numbers in brackets indicate the cycles of electropolymerizing scans.

complex before the electrochemical reaction. Then the electrochemical oxidation of the Co(II) compound to an Co(III) species in Equation 2 was probably rapid. This was followed by a slow chemical step (Eq. 3) involving the rupture of the Co-S bond in the adduct, which also served to generate the Co(II) form of CoTAPc. The thyl radical then reacted very rapidly in Equation 4 to form the disulphide.

### 3.2. Effect of the Thickness of the Poly-CoTAPc Film

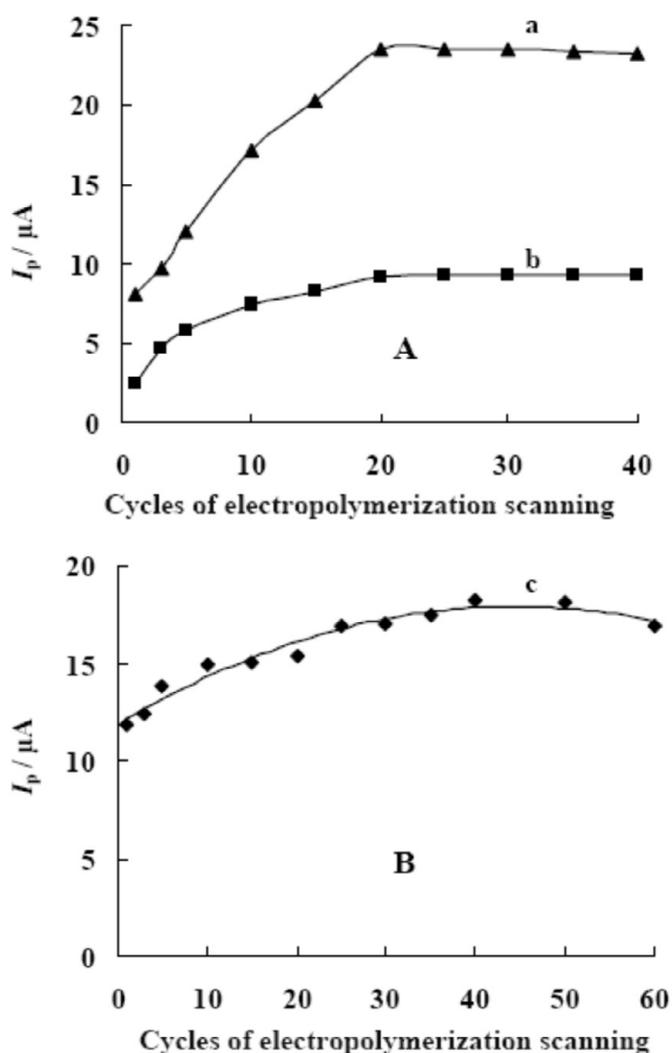
Absolute data on the thickness were not measured; however, the thickness was known to be controlled most simply by varying the cycles of electropolymerization scanning. The film thickness was supposed to be proportional to the scanning cycles of the polymerization.<sup>44,67–68</sup> In our previous work,<sup>69</sup> simultaneous piezoelectric microgravimetry and cyclic voltammetry measurements at an electrochemical quartz crystal microbalance have been used to monitor the growth of poly-CoTAPc film during potential cycling. The results indicated that the thickness of poly-CoTAPc films increased with the cycles of electropolymerizing scans.

Figure 4 shows that for each complex the modified electrodes exhibited cyclic voltammograms with similar shapes. In addition, the amount of electroactive redox cobalt complex sites can be estimated from the electrical charge under the oxidative (or reductive) Co(III)/Co(II) peak, and the peak currents increased with the cycles of electropolymerizing scans, which indicated that the amount of electroactive redox cobalt complex sites increased with the cycles of electropolymerizing scans. Thus, the total number of apparent electroactive sites calculated from cyclic voltammetry experiments at 0.6 V s<sup>-1</sup> gave  $1.06 \times 10^{-9}$  mol cm<sup>-2</sup> and  $3.86 \times 10^{-9}$  mol cm<sup>-2</sup> for 20 and 40 cycles of electropolymerizing scans, respectively.

In Fig. 5, the results indicated 20 and 40 cycles of electropolymerization scanning provided the optimum polymeric film thickness for 6MP and MBI, respectively, and a layer of greenish blue film was obtained.

### 3.3. Effect of pH on Catalytic Behaviour

All in the Fig. 6 showed 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



**Figure 5** Effect of film thickness (cycles of electropolymerization scanning) on the catalytic reduction (a) and oxidation (b) peak currents of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> 6MP in pH = 8.0 PBS (A), and on the catalytic oxidation (c) peak currents of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> MBI in pH = 2.0 PBS (B) at the poly-CoTAPc modified electrode; scan rate = 60 mV s<sup>-1</sup>.

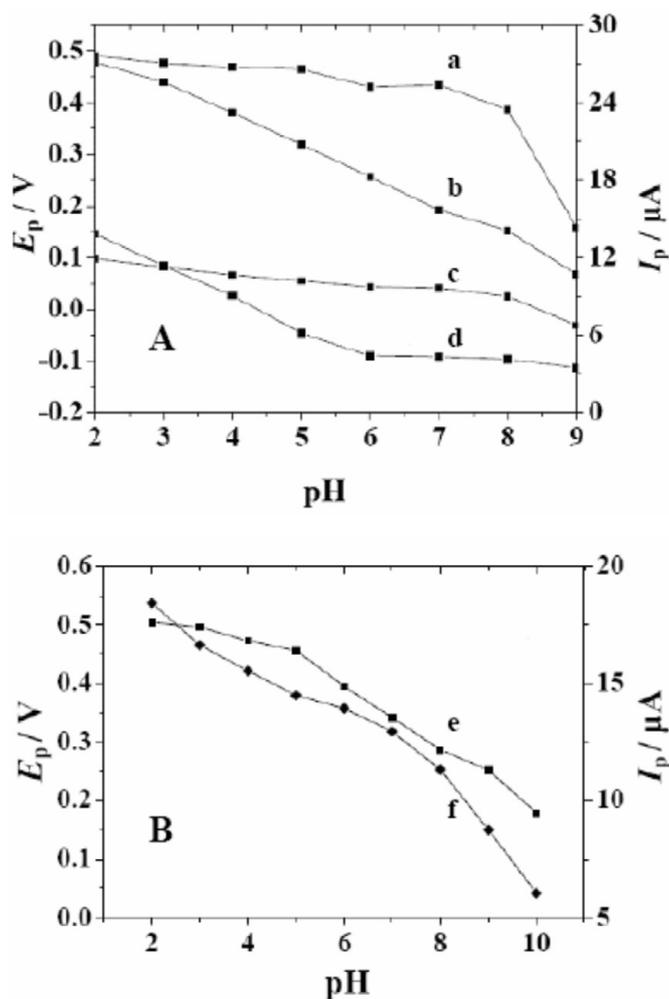


Figure 6 Effect of pH on the peak current and potential of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  6MP (A) and MBI (B) (a:  $I_p/\mu\text{A}$ ; b:  $E_p/\text{V}$ ; c:  $I_p/\mu\text{A}$ ; d:  $E_p/\text{V}$ ; e:  $E_p/\text{V}$ ; f:  $I_p/\mu\text{A}$ ), at the poly-CoTAPc modified electrode, scan rate =  $60 \text{ mV s}^{-1}$ .

studied. Therefore, a pH value of 2.0 was optimum for improving RSH stability and current response.

### 3.4. Effect of Scan Rate on Oxidation and Reduction Peak Current

The intensities of the oxidation and reduction peaks related to the thiols redox processes vary linearly with the square root of potential scan rate in the studied range (Fig. 7), which indicated that the oxidation of RSH and reduction of the corresponding oxidation product at the poly-CoTAPc film electrode were diffusion-controlled over the scan rate range.<sup>51,64</sup>

### 3.5. Stability of Film

To ensure the method was performed appropriately, the system stability was required prior to routine use. In order to determine the stability of the poly-CoTAPc film, the oxidation and reduction peak current responses to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  RSH were recorded 40 times within a day (Fig. 8), the near horizontal line of the graph indicated that the poly-CoTAPc modified electrode was durable (giving 40 determinations without significant loss of response), and our system is 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 films showed they are fit for routine use.

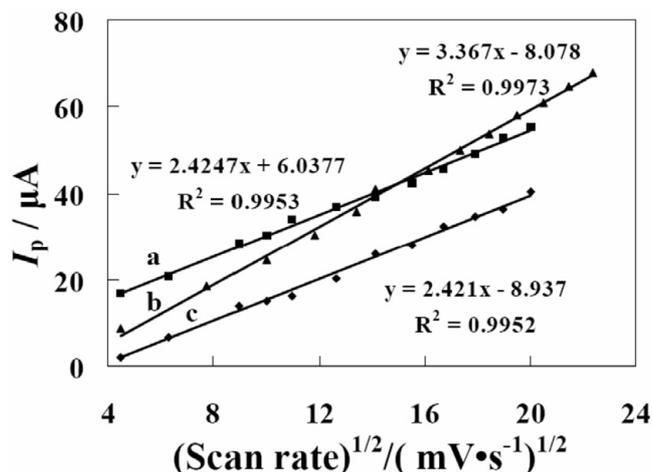


Figure 7. Effect of scan rate on catalytic (a) reduction, (c) oxidation peak current of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  6MP and (b) oxidation peak current of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  MBI at a poly-CoTAPc modified electrode in pH = 2.0 PBS.

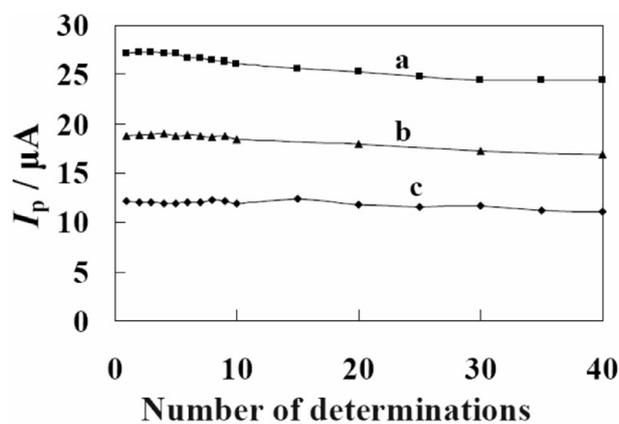
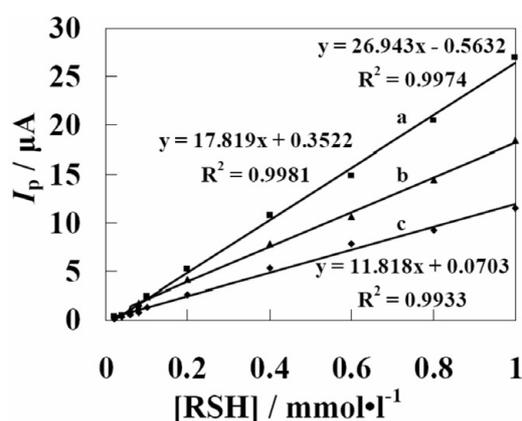


Figure 8 The catalytic reduction (a) and oxidation (b) peak current of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  6MP and oxidation (c) peak current of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  MBI on the number of determinations at the poly-CoTAPc modified electrode, in pH = 2.0 PBS, scan rate =  $60 \text{ mV s}^{-1}$ .

### 3.6. Linearity and Detection Limits for RSH

The oxidation and reduction peak current was chosen as the quantitative measure. There was a good linear relationship between peak current and concentration. To determine the linear calibration curve, correlation coefficient and detection limit of RSH at the poly-CoTAPc film electrode, a series of RSH solutions were tested in pH = 2.0 PBS at  $60 \text{ mV s}^{-1}$ . The intensity of the reduction (Fig. 9a) and oxidation (Fig. 9b) peak was directly proportional to the concentration of 6MP in the concentration range from  $2.0 \times 10^{-5}$  to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  at poly-CoTAPc film modified electrodes. The intensity of the oxidation peak was directly proportional to the concentration of MBI (Fig. 9c) in the concentration range from  $6.0 \times 10^{-5}$  to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  at poly-CoTAPc film modified electrodes. The linear variations were obtained between concentration and peak current rendering use of this calibration curve useful for quantitative analysis of RSH. Moreover, the peak potential RSH oxidation shifted to more positive value and the peak current enhanced upon increasing the concentration of RSH (not shown). In fact, these observations indicate an interaction of RSH with metal central of CoTAPc. At poly-CoTAPc film modified electrode, the detection limit of 6MP is estimated to be  $5.0 \times 10^{-8} \text{ mol L}^{-1}$  and  $2.0 \times 10^{-7} \text{ mol L}^{-1}$  with oxidation and reduction current peak as the quanti-



**Figure 9** Effect of concentration on catalytic reduction (a) and oxidation (b) peak current for 6MP and oxidation (c) peak current for MBI at a poly-CoTAPc modified electrode in pH = 2.0 PBS, scan rate = 60 mV s<sup>-1</sup>.

tative measure in terms of the role of signal to noise ratio of 3:1 (S/N = 3), respectively. At poly-CoTAPc film modified electrode, the detection limit of MBI is estimated to be  $1.0 \times 10^{-7}$  with oxidation peak current as the quantitative measure in terms of the role of signal to noise ratio of 3:1 (S/N = 3). Comparing the detection limit in this work with those obtained in the literature, the sensitivity of the present work is higher than those by the spectrophotometric method<sup>70</sup>, simple chemiluminescence method<sup>18</sup> and cathodic stripping voltammetric determination<sup>38</sup>. On the other hand, although the sensitivity is a little lower than some other methods, such as HPLC coupled to electrochemical detector<sup>15</sup>, fluorescence method enhancement of Au nanoparticles<sup>16</sup> and chemiluminescence method<sup>17</sup>, the proposed technique is simple and convenient, low cost and sufficiently sensitive for the determination of the compounds of interest.

### 3.7. Interferences and Application

The effect of some possible interferences commonly found in urine were investigated using voltammetric determination. The results showed that the common inorganic ions (such as: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc.) 100 times as much as RSH concentration, did not preclude the use of the electrode to analyze RSH. Other organic compounds such as glucose ( $1.0 \times 10^{-2}$  mol L<sup>-1</sup>) and urea ( $1.0 \times 10^{-2}$  mol L<sup>-1</sup>) also did not interfere the determination. Ascorbic acid ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) can slightly interfere the determination if it was present.

The proposed method was applied to determinate RSH in spiked human urine. The urine samples, obtained from healthy volunteers, were spiked with RSH at different concentrations, and treated as the section 2.4 described. The recoveries from human urine were measured by spiking drug-free human urine with known amounts of RSH. The concentrations of RSH 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 97.6–103.2 % (RSD = 0.96–7.76 %) with the oxidation peak current as the quantitative measure, and 95.0–100.3 % (RSD = 1.24–4.53 %) with the reduction peak current as the quantitative measure for 6MP. The recovery for MBI was in the range of 94.3–109.4 % (RSD = 3.45–5.36 %) with the oxidation peak current of as the quantitative measure. The results revealed that this proposed method has good accuracy and promising application.

### 4. Conclusions

The poly-CoTAPc film modified electrode was prepared by eletropolymerization on the GCE. The poly-CoTAPc film could

enhance the catalytic role of the electron mediator, which can lower the overpotential and increase the sharpness and current of redox peak of 6MP and MBI in acidic solution (pH = 2); In addition, the film modified electrodes show many advantages such as relatively long-term operational stability, durability, high sensitivity, reproducible responses and a wide linear range of the calibration plot for the determination of 6MP and MBI. In this sense, the above advantages together with ease of preparation make the poly-CoTAPc film modified electrode a useful amperometric detector for 6MP and MBI.

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