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Electrochemical metal-ion sensor based on a cobalt phthalocyanine complex captured in Nafion[®] on a glassy carbon electrode

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This article describes an electrochemical metal-ion sensor based on a cobalt phthalocyanine (CoPc) complex and determination of its sensor activity for some transition metal ions. Ag⁺ and Hg²⁺, among several transition metal ions, coordinate to the sulfur donors of CoPc and alter the electrochemical responses of CoPc in solution, indicating possible application of the complex as Ag⁺ and Hg²⁺ sensor. For practical application, CoPc was encapsulated into a polymeric cation exchange membrane, Nafion, on a glassy carbon electrode and used as an electrochemical coordination element. This composite electrode was potentiometrically optimized and potentiometrically and amperometrically characterized as transition metal-ion sensors with respect to reproducibility, repeatability, stability, selectivity, linear concentration range, and sensitivity. A $\mu\text{mol dm}^{-3}$ sensitivity of the CoPc-based sensor indicates its possible practical application for the determination of Ag⁺ and Hg²⁺ in waste water samples.

Keywords: Cobalt phthalocyanine; Nafion; Electrochemical sensor; Electrochemistry; Metal ion

1. Introduction

Industrial development is associated with emission of toxic substances, such as pesticides, toxic organic compounds, and heavy metals. [1]. Due to the potential impact of metal ions on human health and environment, sensitive methods of detection are widely sought [2]. Environmental monitoring requires rugged sensors for detection of pollution and toxic chemicals, and automated and continuous, remote and *in situ* monitoring will be increasingly required. Converting the sensing information to an easily processed electronic signal is challenging due to the complexity of connecting an electronic device directly to the target environment. Electrochemical sensors provide an attractive means to analyze the content of a target sample due to the direct conversion of an event to an electronic signal. Electrochemical biosensors are at the forefront of a multidisciplinary science combining electrochemistry and biology [3]. Due to potential technological applications in the bioanalytical and environmental

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fields, tremendous attention has been concentrated to electrochemical molecular recognition, which is a rapid growing research field of supramolecular science [4–8]. The aim of this field is the development of new receptors, capable to modify selectively their electrochemical responses upon interactions with target species. These molecular systems should contain two components: (i) one electro-active group (antenna) and (ii) binding sites specially designed for the specific guest.

Metallophthalocyanines (MPcs) carry both binding sites and attractive functional antennas due to their excellent electrochemical properties, which can be adjusted by suitable metal center and substituents. Phthalocyanines have attracted interest as advanced materials due to their remarkable properties that include flexibility, chemical, and thermal stabilities [9]. Due to these versatile properties, MPcs were used as optic and electrochemical sensors. As stated by Stillman, optical properties of the phthalocyanines are dominated by the π – π^* bands associated with the heteroaromatic, 16 atom, 18 π –electron inner perimeter cyclic polyene. The 18 π –electron system of the Pc ring also governs the redox properties of the complexes [9]. Stillman reported spectral data for many neutral porphyrin and phthalocyanine compounds with a range of metals, axial, and peripheral substituents from absorption and magnetic circular dichroism techniques and illustrated effect of metal center, substituents, and the reduction and/or oxidation processes to spectra of MPcs [9, 10]. Similarly Lukyanets and coworkers stated that peripherally substituted phthalocyanines with alkyl-, aryl-, or hetaryl substituents, halogens, thiols, amines, ethers, and other groups are currently used as industrial functional materials in various applications. The majority of these applications take advantage of the unique optical (specifically low-energy Q-band) and redox properties of phthalocyanines which can be fine-tuned using appropriate peripheral substituents [11, 12]. Lukyanets also stated that peripheral substituents can be used as an anchor or bridging group for formation of controlled supramolecular assemblies and similar applications (i.e. heterogenization of catalysts) [11, 12]. Substituents of MPcs carrying O, N, and S behave as binding sites and form stable complexes with transition metal ions [13–20]. In previous papers, we synthesized various MPcs peripherally substituted with different functional groups and investigated the electrochemical, electrocatalytic, electrochromic, and metal sensing properties of these complexes [21–24]. In these papers, we demonstrated that sulfur containing substituent of MPcs acted as binding groups for heavy transition metal ions, thus these MPcs were used as optical metal sensors in solution [23, 24]. Interaction of metal ions with MPcs was monitored by following the change of the Q-bands. Changing the Q-band of MPcs altered the electron transfer processes of the MPc complexes [9, 10]. These responses of MPcs are the desired properties for electrochemical sensors.

In our previous sensor studies, we have used MPc bearing crown ether substituents as electrochemical metal sensors for alkali metal ions in solution. In these studies, interaction of alkali metal ions with the crown ether of the MPcs altered the electron transfer properties of the MPc complexes. There are similar papers in the literature on alkali metal-ion sensor properties of MPcs bearing crown ether substituents [25–27]. In this article, we investigate the electrochemical transition-metal-ion sensor activities of a cobalt phthalocyanine (CoPc) bearing sulfur binding groups [28] (figure 1). Sensor activity of CoPc captured in Nafion on a glassy carbon electrode has been investigated with cyclic voltammetry (CV), square wave voltammetry (SWV), and double potential step chronoamperometry (DPSCA) techniques.

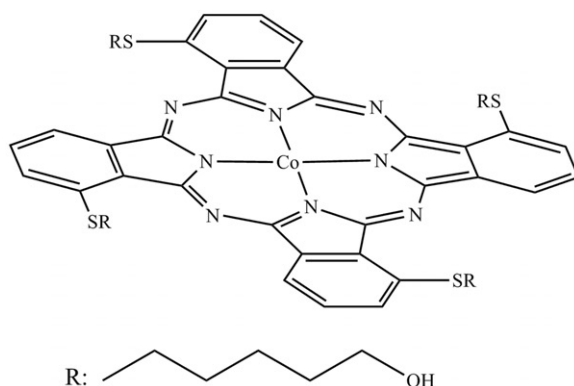


Figure 1. Structure of tetrakis(6-hydroxyhexylthio) cobalt phthalocyanine.

2. Experimental

2.1. Reagents and instrumentation

All chemicals were of analytical reagent grade. A 25% alcohol solution of Nafion[®], dimethyl sulfoxide (DMSO), tetrabutylammoniumperchlorate (TBAP), CuSO₄, Ni(CH₃COO)₂, Co(CH₃COO)₂, Pb(NO₃)₂, AgNO₃, Hg(NO₃)₂, CdCl₂, and LiClO₄ were bought from Sigma-Aldrich, Germany. CoPc (tetrakis(6-hydroxyhexylthio)cobalt phthalocyanine (figure 1)) was synthesized as reported earlier [28]. All sensor applications were performed in aqueous solution containing 0.10 mol dm⁻³ LiClO₄ as supporting electrolyte. Ultrapure water obtained from a Millipore water purification system (≥ 18 M Ω , Milli-Q, Millipore) was used in all runs.

CV, SWV, and DPSCA measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25°C. The working electrode was bare and modified glassy carbon electrodes with a surface area of 0.071 cm². A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge.

2.2. Preparation of composite electrodes

Prior to modification, the GCE was polished on a polishing cloth with diamond slurry and rinsed thoroughly with ultrapure water, followed by sonicating in ethanol and ultrapure water, successively. Then the electrode was allowed to dry at room temperature. Cast film technique was carried out for preparation of the composite electrodes as follows. Two different kinds of the composite electrode were prepared. For the first kind, only CoPc was casted on the GCE, abbreviated as GCE/CoPc. For the second kind, CoPc was retained into Nafion on the GCE and abbreviated as GCE/Nf/CoPc. During preparation, 10.0 μ L of a mixture of 5.0 μ L 5.0 wt% alcoholic Nafion solution and 5.0 μ L 1.0×10^{-3} mol dm⁻³ CoPc in DMSO (only CoPc for the GCE/CoPc electrode) was cast on a GCE by solvent evaporation under vacuum. Then the modified electrode was dried at room temperature, washed with distilled water,

and finally dried under vacuum and kept in a 0.1 mol dm^{-3} LiClO_4 aqueous solution. ITO/CoPc and ITO/Nf/CoPc electrodes were also prepared for spectral measurements.

2.3. Sensor properties of composite electrodes

To find the possible interaction of CoPc with transition metal ions, CV, and SWV of CoPc in DMSO/TBAP electrolyte system were carried out without metal ions and with gradual addition of 1.0 mmol dm^{-3} metal ions. Then sensor measurements of the modified electrodes (GCE/Nf/CoPc) were carried out in aqueous solution with the SWV and DPSCA techniques. During measurements in the solid state, an adequate number of SWV cycles were applied to reach the steady state and then, metal-ion solutions were added to the aqueous solution gradually. After efficient stirring, SWVs and CVs were recorded. DPSCA measurements were carried out by following the same procedure under the applied constant potentials (one for the reduction and a second for oxidation of the GCE/Nf/CoPc electrode) by using freshly prepared electrodes. During DPSCA measurements, current density of the electrodes was recorded as a function of time of the applied potentials.

3. Results and discussion

3.1. Interaction of CoPc with metal ions in solution

To investigate the electrochemical responses of the interaction between CoPc and transition metal ions, CoPc dissolved in DMSO/TBAP electrolyte system is titrated with some transition metal ions (Ag^+ , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Hg^{2+} , and Cd^{2+}). Voltammetric responses of these titration experiments indicate interaction of Ag^+ (figure 2) and Hg^{2+} (figure 3) with CoPc, while Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} did not change the redox responses of CoPc in solution.

Figure 2 shows the CV and SWV responses of CoPc during titration with Ag^+ in the DMSO/TBAP electrolyte system. As shown in this figure, CoPc gives an oxidation couple at 0.32 V and a reduction couple at -0.54 V without Ag^+ . During titration with Ag^+ , CV of the system starts to change due to the interaction of CoPc with Ag^+ . While the cathodic wave of the reduction couple shifts to negative potentials, a new wave is recorded during the anodic scan. Observation of a new anodic wave at just negative side of the previous anodic wave causes splitting of the anodic process. Splitting of the anodic wave and shifting of the cathodic one could be easily assigned to aggregation of the monomeric CoPc due to the interaction with Ag^+ . In previous papers, we studied interaction of various MPcs with different transition metal ions spectroscopically [23, 24, 28]. It is well documented in these papers and similar papers in the literature that some transition metals form coordination bonds with sulfur of the substituents of MPcs. Formation of the aggregate decreased the intensity of the Q-band of the monomeric species and caused formation of new bands at different wavelengths assigned to aggregates [25–27, 29]. With the help of these data, we have proposed that changing of the position of the Q-band of the complexes due to interaction with transition metal ions probably alters the redox behavior of the MPcs. Voltammetric responses of the interaction of CoPc with Ag^+ supports this proposition. As shown in

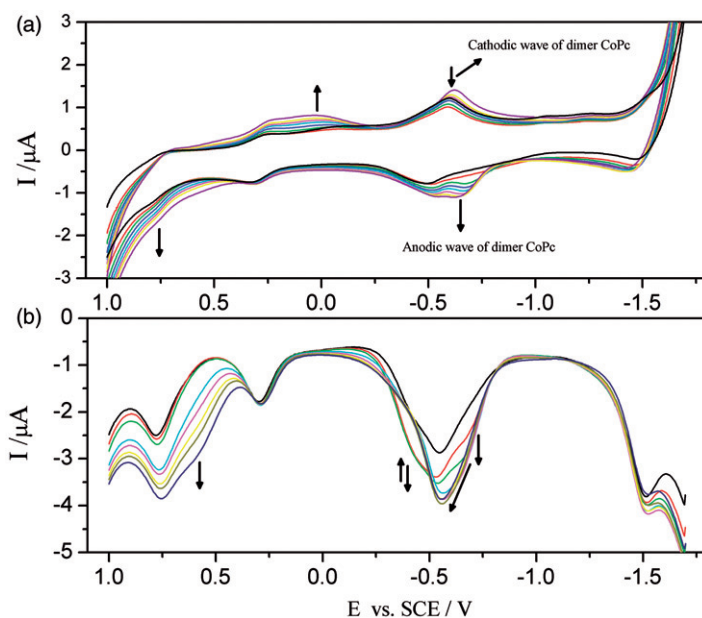


Figure 2. (a) CV and (b) SWV responses of CoPc during titration with Ag^+ on Pt in DMSO/TBAP electrolyte system. (The black arrows show the direction of change of CV and SWV responses with respect to $2 \mu\text{mol dm}^{-3} \text{Ag}^+$ addition.)

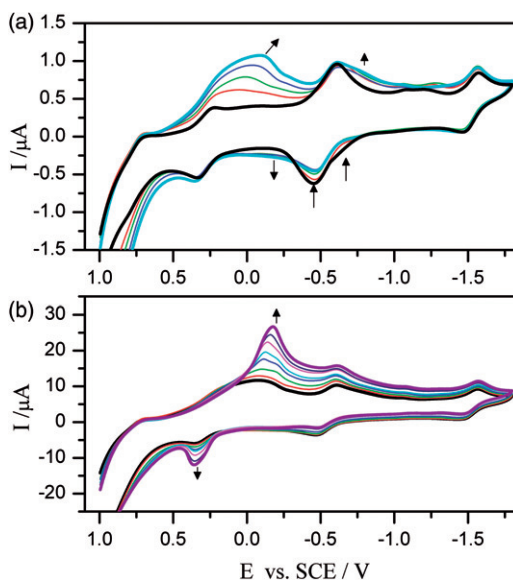


Figure 3. CV responses of CoPc during titration with Hg^{2+} on Pt in DMSO/TBAP electrolyte system: (a) $2 \mu\text{mol dm}^{-3} \mu\text{L}$ gradual addition of Hg^{2+} until $52 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$; and (b) gradual addition of Hg^{2+} after $52 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$. (The black arrows show the direction of change of CV responses with respect to $2 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$ addition.)

figure 2(a), addition of Ag^+ to the CoPc solution results in a new electron transfer process at the negative side of the redox processes of the CoPc. These changes in the CV of CoPc indicate interaction of Ag^+ with CoPc. SWV of CoPc shown in figure 2(b) indicates the changes more obviously and supports the CV responses during the interaction of CoPc with Ag^+ .

Figure 3 represents CVs of CoPc during titration with Hg^{2+} . Two distinct voltammetric changes are recorded during this titration. Until $52.0 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$ addition (figure 3a), new redox waves are recorded before or after the redox couples of CoPc. Especially, the cathodic waves at -0.09 V and -0.80 V and the anodic waves at -0.20 V and -0.71 V are more apparent, while waves of CoPc decrease in current intensity. These voltammetric data indicate coordination of Hg^{2+} with the sulfur atoms of CoPc molecules. After $52.0 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$ addition, the previous redox waves of CoPc remain unchanged and two new waves increase at -0.18 V and 0.35 V (figure 3b). These waves are due to electron transfer of excess Hg^{2+} , which did not react with CoPc. Solution containing Hg^{2+} gave similar waves without CoPc during the blank test, which supports the assignments of these waves. SWVs shown in figure 4 illustrate these changes more obviously during titration of CoPc with Hg^{2+} . While the waves assigned to CoPc decrease in current intensity, new waves are recorded, assigned to the aggregates due to the interaction between Hg^{2+} and CoPc. Comparing CV responses, SWV is more sensitive for sensing of Ag^+ and Hg^{2+} among Ag^+ , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , and Hg^{2+} . Many different factors (such as “soft” or “hard” character of the metal cations, different affinity of the binding side of ligand to the various cations, electronic structure of metal cations, ionic radius of the cations, and porosity and firmness of the film on the composite electrodes) may affect selectivity of

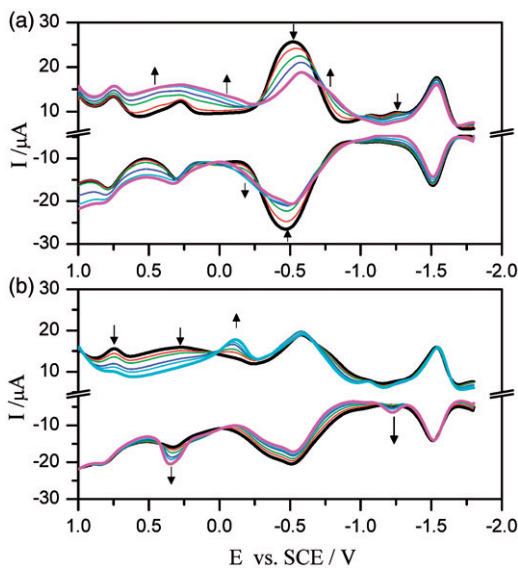


Figure 4. SWV responses of CoPc during titration with Hg^{2+} on Pt in DMSO/TBAP electrolyte system: (a) $2 \mu\text{mol dm}^{-3} \mu\text{L}$ gradual addition of Hg^{2+} until $52 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$; and (b) gradual addition of Hg^{2+} after $52 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$. (The black arrows show the direction of change of SWV responses with respect to $2 \mu\text{mol dm}^{-3} \text{Hg}^{2+}$ addition.)

a ligand to the specific target species and can govern interaction of a metal ion with a ligand. The ability of an ion to coordinate water with flexible coordination is thought to be an important factor for selectivity of a ligand [30].

3.2. Metal-ion sensing measurements in solid state

Solution titration of CoPc showed that interaction of metal ions with CoPc altered the redox properties of CoPc. This distinctive property of the complex represented possible metal-ion sensor activity of CoPc only for Ag^+ and Hg^{2+} in solution. For practical sensor applications, CoPc should be coated on an electrode and its solid state on the electrode should interact with the target species. Thus, composite electrodes based on CoPc were prepared and tested for possible metal-ion sensing application.

Two different composite electrodes (GCE/CoPc and GCE/Nf/CoPc) were prepared and tested for sensing measurements. First, CV and SWVs responses of GCE/CoPc electrode were recorded with increasing metal-ions concentration. Addition of Ag^+ and Hg^{2+} did not change the response of this electrode until $25 \mu\text{mol dm}^{-3}$ ion addition, after this point, an electrochemical response was recorded, which is similar to the one recorded during the blank test. These voltammetric data indicate that CoPc did not interact with Ag^+ and Hg^{2+} ions, when CoPc was coated on GCE alone. When CoPc was dispersed in Nafion on GCE, GCE/Nf/CoPc composite electrode, CoPc interacts with Ag^+ and Hg^{2+} . This different behavior of CoPc on different composite electrodes may be due to different orientations of CoPc molecules on GCE electrode and/or different porosity and firmness of CoPc films on these two composite electrodes. Most probably, the metal ions did not penetrate into the film on the GCE/CoPc composite electrode, thus these ions could not be coordinated with the CoPc on the GCE/CoPc electrode. Using Nafion on GCE may supply a region for CoPc to reorient and for the ions to penetrate between CoPc molecules. We propose that when CoPc molecules are captured in the Nafion film, CoPc molecules behave as separate monomers and are not in aggregated form. However, when they coated directly on GCE, they form a stable, immobile, and firm film. To clarify that CoPc is not aggregated in Nafion, UV-Vis spectra of the ITO/CoPc and ITO/Nf/CoPc were recorded (figure 5). While ITO/CoPc

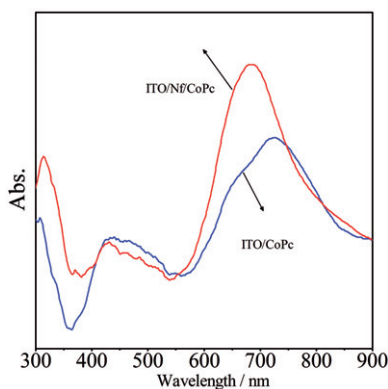


Figure 5. UV-Vis spectrum of ITO/CoPc and ITO/Nf/CoPc electrodes.

gives the Q-band at 680 nm in addition to the band at 730 nm assigned to aggregation of CoPc in solid state, ITO/Nf/CoPc gave only the Q-band at 680 nm similar to spectra recorded in solution. These spectral data indicated that CoPc was not in aggregated form when dispersed in Nafion.

GCE/Nf/CoPc composite electrodes were prepared by a drop-drying technique. Before SWV sensing measurement, repetitive SWV cycles were performed to obtain a stable film on the electrodes. SWV of the electrodes changed during the repetitive SWV cycles and reached a steady state after 10 SWV cycles. To investigate electrochemical reaction of metal ions with CoPc in the solid state, SWVs of GCE/Nf/CoPc electrode were recorded without and with increasing metal-ion concentration. While GCE/Nf/CoPc electrodes did not give any responses to addition of Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} , GCE/Nf/CoPc electrode behaves as a sensor for Ag^+ and Hg^{2+} ions selectively in solid state.

Figure 6 represents SWV responses of GCE/Nf/CoPc electrodes in aqueous LiClO_4 solution during gradual addition of Ag^+ . To investigate responses of both reduction and oxidation processes, cathodic SWV (figure 6a; $E_i = 1.00$ V; $E_f = -0.85$ V) and anodic SWV (figure 6b; $E_i = -0.85$ V; $E_f = 1.00$ V) scans were sequentially performed without interruption. The GCE/Nf/CoPc electrode gives a peak at 0.10 V followed with a small wave at -0.33 V during the cathodic potential scan and gives two anodic waves at 0.13 V and 0.55 V during the sequential anodic scan without Ag^+ . When $2.0 \mu\text{mol dm}^{-3}$ Ag^+ is gradually added, both the anodic and cathodic waves change with increasing Ag^+ concentration. During the cathodic scans, the redox wave of CoPc at 0.10 V decreases in current intensity with the positive potential shift and reaches steady state after $48 \mu\text{mol dm}^{-3}$ Ag^+ addition. The wave at -0.33 V disappears immediately after $6 \mu\text{mol dm}^{-3}$ Ag^+ addition. During the anodic scan, while the wave at 0.14 V remains stable, the wave at 0.55 V decreases gradually in current intensity with a negative potential shift until $48 \mu\text{mol dm}^{-3}$ Ag^+ addition. After this point, while all waves attributed to the GCE/Nf/CoPc electrode remain stable, a sharp wave is recorded at 0.22 V with increasing current intensity during further Ag^+ addition. A blank test (SWV responses of the bare GCE to Ag^+ addition) was performed to assign the nature

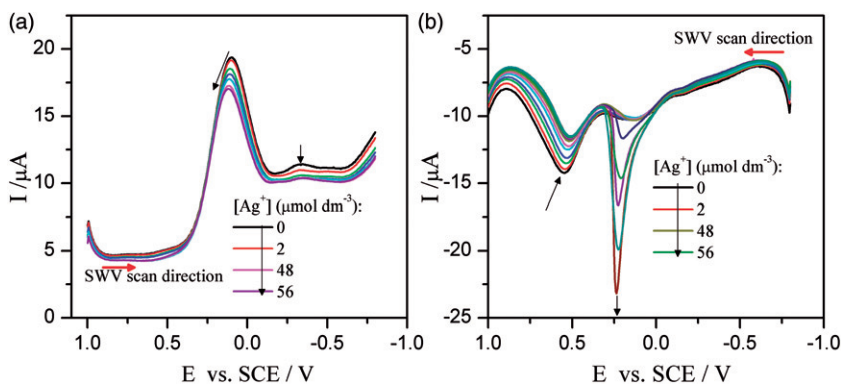


Figure 6. SWV responses of GCE/Nf/CoPc electrodes during gradual addition of Ag^+ to the aqueous solution. SWV parameters: (a) $E_i = 1.00$ V; $E_f = -0.85$ V; pulse size = 100 mV; step size = 5 mV; frequency: 25 Hz, and (b) $E_i = -0.85$ V; $E_f = 1.00$ V; pulse size = 100 mV; step size = 5 mV; frequency: 25 Hz. (The black arrows show the direction of change of SWV responses with respect to $2 \mu\text{mol dm}^{-3}$ Ag^+ addition.)

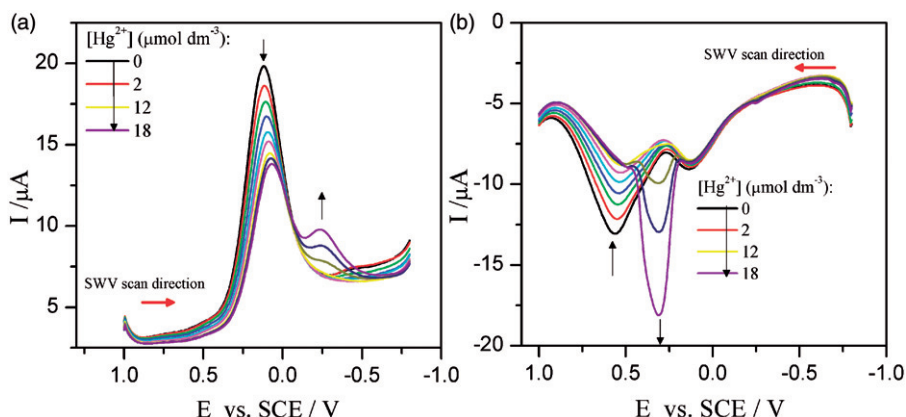


Figure 7. SWV responses of GCE/Nf/CoPc electrodes during gradual addition of Hg^{2+} to the aqueous solution. SWV parameters: (a) $E_i = 1.00 \text{ V}$; $E_f = -0.85 \text{ V}$; pulse size = 100 mV ; step size: 5 mV ; frequency: 25 Hz , and (b) $E_i = -0.85 \text{ V}$; $E_f = 1.00 \text{ V}$; pulse size = 100 mV ; step size: 5 mV ; frequency: 25 Hz . (The black arrows show the direction of change of SWV responses with respect to $2 \mu\text{mol dm}^{-3} \text{ Hg}^{2+}$ addition.)

of the wave at 0.22 V . A similar anodic sharp wave at 0.20 V and a cathodic broad wave at -0.20 V were recorded on the bare GCE during gradual addition of Ag^+ to the aqueous solution. Thus, the wave recorded on the GCE/Nf/CoPc electrode at 0.22 V is easily attributed to oxidation of silver which accumulated during the cathodic electroreduction of excess Ag^+ which did not interact with CoPc. These voltammetric results indicate sensor activity of GCE/Nf/CoPc electrode between 2 and $48 \mu\text{mol dm}^{-3} \text{ Ag}^+$.

Figure 7 represents SWV responses of GCE/Nf/CoPc electrodes during gradual addition of Hg^{2+} . Titrations of CoPc with Hg^{2+} and Ag^+ give similar voltammetric changes. When Hg^{2+} concentration is gradually increased, both anodic and cathodic waves decrease in current intensity with a potential shift and reach a steady state after $12 \mu\text{mol dm}^{-3} \text{ Hg}^{2+}$ addition. However the cathodic wave recorded at 0.10 V shifts to negative potentials, while it shifts to positive potentials during titration with Ag^+ . After $12 \mu\text{mol dm}^{-3} \text{ Hg}^{2+}$ addition, while the anodic waves attributed to the GCE/Nf/CoPc electrode remain as unchanged, a sharp wave assigned to electron transfer reaction of the excess mercury is recorded at 0.31 V with increasing current intensity during further Hg^{2+} addition. These data indicate the application of this electrode as Hg^{2+} sensor within 2 – $12 \mu\text{mol dm}^{-3} \text{ Hg}^{2+}$ concentration.

Response of the GCE/Nf/CoPc electrode was also investigated in the presence of mixture of all ions and the presence of both Ag^+ and Hg^{2+} . For this experiment, the titration was performed with the solution containing equal molarity of each ion present. In the presence of both Ag^+ and Hg^{2+} , the responses of GCE/Nf/CoPc electrode are given in figure 8. As shown in this figure, while the cathodic response of the electrode is very similar to the response of Ag^+ ion (figure 8a), anodic responses are completely different (figure 8b). Until $30 \mu\text{mol dm}^{-3}$ mixture of Ag^+ , Hg^{2+} , the peak 0.56 V shifts slightly to negative potentials. These changes are very similar to the changes recorded for only Ag^+ . After this point, while a cathodic wave is recorded at -0.12 V , two sharp waves are recorded at 0.22 and 0.31 V with increasing current intensity during further addition of the Ag^+ and Hg^{2+} mixture. When compared with the responses of Ag^+ (figure 6) and Hg^{2+} (figure 7) present alone, it is obvious that the wave at 0.22 V is

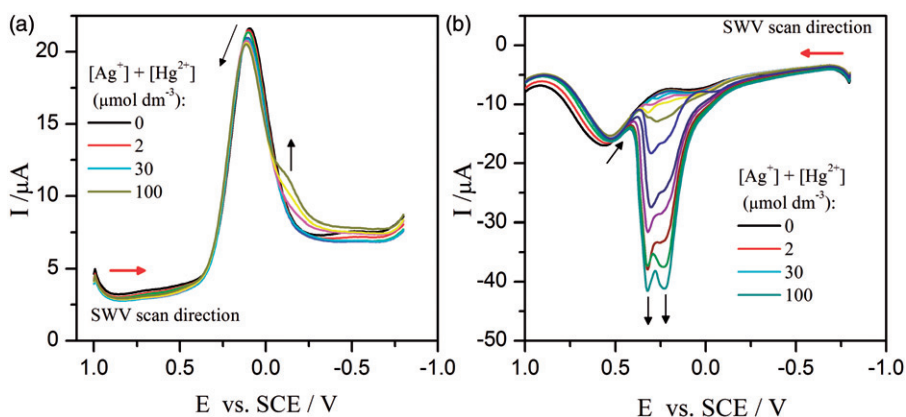


Figure 8. SWV responses of GCE/Nf/CoPc electrodes during gradual addition of the mixture of Ag^+ and Hg^{2+} to the aqueous solution. SWV parameters: (a) $E_i = 1.00 \text{ V}$; $E_f = -0.85 \text{ V}$; pulse size = 100 mV ; step size: 5 mV ; frequency: 25 Hz , and (b) $E_i = -0.85 \text{ V}$; $E_f = 1.00 \text{ V}$; pulse size = 100 mV ; step size: 5 mV ; frequency: 25 Hz . (The black arrows show the direction of change of SWV responses with respect to $2 \mu\text{mol dm}^{-3}$ addition.)

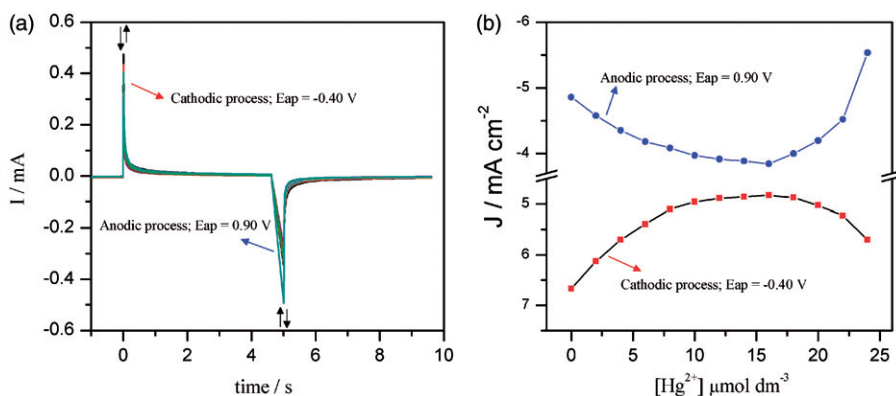


Figure 9. DPSCA responses of GCE/Nf/CoPc electrode during gradual addition of Hg^{2+} to the aqueous solution: (a) current vs. time graph, and (b) Hg^{2+} sensing calibration curves derived from DPSCA responses of GCE/Nf/CoPc electrode.

overlapped with Ag^+ and the wave at 0.22 V is overlapped with Hg^{2+} . The presence of other metal ions in the mixture did not affect the responses of the electrode recorded with the presence of both Ag^+ and Hg^{2+} .

3.3. DPSCA sensing measurements

The interaction of GCE/Nf/CoPc with Ag^+ and Hg^{2+} were also performed with DPSCA. By using this technique, both reduction and oxidation responses of GCE/Nf/CoPc electrode to gradual addition of Ag^+ and Hg^{2+} could be followed amperometrically. Figure 9 represents the DPSCA responses of GCE/Nf/CoPc electrode in the LiClO_4 aqueous solution during gradual addition of Ag^+ . Both cathodic and anodic current densities decrease gradually with increasing Ag^+ concentration until

48 $\mu\text{mol dm}^{-3}$ Ag^+ addition. After this point, while the cathodic current decreases slightly, anodic current increases sharply due to oxidation of excess silver. While the cathodic process gives a linear response between 2 and 10 $\mu\text{mol dm}^{-3}$ Ag^+ with a sensitivity of $0.42 \text{ A cm}^{-2} (\text{mol L}^{-1})^{-1}$, the anodic process gives a linear response between 2 and 28 $\mu\text{mol dm}^{-3}$ Ag^+ with a sensitivity of $0.43 \text{ A cm}^{-2} (\text{mol L}^{-1})^{-1}$.

Figure 9 represents DPSCA responses of GCE/Nf/CoPc electrode during gradual addition of Hg^{2+} to the aqueous solution. Hg^{2+} and Ag^+ give very similar DPSCA responses. As shown in figure 9, both cathodic and anodic current densities decrease gradually with increasing Hg^{2+} concentration until 12 $\mu\text{mol dm}^{-3}$ Hg^{2+} addition. After this point, both cathodic and anodic current intensities increase sharply due to electron transfer of the excess mercury. While cathodic process gives a linear response between 2 and 8 $\mu\text{mol dm}^{-3}$ Hg^{2+} with a sensitivity of $2.76 \text{ A cm}^{-2} (\text{mol L}^{-1})^{-1}$, anodic process gives a linear response between 2 and 12 $\mu\text{mol dm}^{-3}$ Ag^+ with a sensitivity of $1.6 \text{ A cm}^{-2} (\text{mol L}^{-1})^{-1}$.

Background (“blank”) experiments with GCE/Nf/CoPc electrode were tested before and after the sensing experiments. The CV and SWV responses of GCE/Nf/CoPc electrode did not change during the sequential scans without metal ion addition, which indicates stability of the electrode in solution under the potential scan between -1.0 and 1.0 V. After sensing measurements, a blank test was also performed in aqueous solution without metal ions. During sequential scans, the CV and SWV responses of the GCE/Nf/CoPc electrode follow the reverse of the trend recorded during sensing measurements. To regenerate the original response of the system, the GCE/Nf/CoPc electrode was washed with water in an ultrasound water bath. After washing, approximately 90% of the GCE/Nf/CoPc electrode was regenerated. However, it does not completely turn to the CV of the unused GCE/Nf/CoPc electrode. Reuse of this electrode gives similar responses to the metal ions during the sensing measurements.

4. Conclusion

Although numerous electrochemical metal-ion biosensors generally based on the immobilization of the redox proteins and mediators have been reported, an enzymeless/mediatorless metal-ion sensor based on CoPc has been developed in this study. Value of phthalocyanines as sensors comes from their versatile structure, because functional groups, e.g. soft metal binder sulfurs, on the substituents and redox active metal center of MPcs behave as binding sites for different target species. Interaction of target species, e.g. metal ions, with the binding sides of MPcs alters the electrochemical response of the MPcs, which are used as a mediator element. Therefore, substituent-functionalized MPcs bearing redox active metal centers are expected to exhibit interesting electrochemical behavior and act as sensors. Another advantage of the phthalocyanines is their remarkable chemical and thermal stabilities. Thus using MPcs as metal-ion sensors instead of both an enzyme and mediators could be a good alternative to the inevitable drawbacks of enzymes and mediators. Electrochemical metal-ion sensor activity of CoPc was investigated in solution and solid state. CoPc forms aggregates with Ag^+ and Hg^{2+} ions in solution, which indicates possible application of the complex as a metal sensor. For practical application, CoPc was immobilized in a polymeric cation exchange membrane, Nafion, on a glassy carbon electrode and used as an electrochemical

receptor for complexation with Ag^+ and Hg^{2+} . This composite electrode was used as potentiometric and amperometric sensors and characterized with respect to reproducibility, repeatability, stability, linear concentration range, and sensitivity for transition metal-ion sensors. SWV results indicate the sensor activity of GCE/Nf/CoPc electrode between 2 and $48 \mu\text{mol dm}^{-3}$ Ag^+ and 2 and $12 \mu\text{mol dm}^{-3}$ Hg^{2+} concentration range. A $\mu\text{mol dm}^{-3}$ sensitivity of the CoPc-based sensor indicates its possible practical application for determination of Ag^+ and Hg^{2+} ions in waste water samples.

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References

- [1] W. Yantasee, Y.H. Lin, K. Hongsirikarn, G.E. Fryxell, R. Addleman, C. Timchalk. *Environ. Health Persp.*, **115**, 1683 (2007).
- [2] F.A. Barile. *Principles of Toxicology Testing*, CRC Press, Boca Raton, FL (2008).
- [3] M. Badihi-Mossberg, V. Buchner, J. Rishpon. *Electroanalysis*, **19**, 2015 (2007).
- [4] P.L. Boulas, M. Gómez-Kaifer, L. Echegoyen. *Angew. Chem., Int. Ed.*, **37**, 216 (1998).
- [5] P.D. Beer. *Acc. Chem. Res.*, **31**, 71 (1998).
- [6] P.D. Beer, D.K. Smith. *J. Chem. Soc., Dalton Trans.*, 417 (1998).
- [7] P.D. Beer, J. Cadman. *Coord. Chem. Rev.*, **205**, 131 (2000).
- [8] H. Plenio, C. Aberle. *Chem. Eur. J.*, **7**, 4438 (2001).
- [9] J. Mack, M.J. Stillman. *Coord. Chem. Rev.*, **219**, 993 (2001).
- [10] M.J. Stillman. In *Handbook of Porphyrin Science*, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), Vol. 14, pp. 461–524, World Scientific Publishing, Singapore (2010).
- [11] V.N. Nemykin, E.A. Lukyanets. *J. Porphyrins Phthalocyanines*, **14**, 1 (2010).
- [12] S.A. Borisenkova, E.G. Girenko, B.G. Gherassimov, L.M. Mazyarkina, V.P. Erofeeva, V.M. Derkacheva, O.L. Kaliya, E.A. Lukyanets. *J. Porphyrins Phthalocyanines*, **3**, 210 (1999).
- [13] H. Plenio, R. Diodone. *Angew. Chem. Int. Ed.*, **33**, 2175 (1994).
- [14] H. Plenio, C. Aberle, Y. Al Shihadeh, J.M. Lloris, R. Martínez-Mañez, T. Pardo, J. Soto. *Chem. Eur. J.*, **7**, 2848 (2001).
- [15] P.D. Beer, N.C. Fletcher, T. Wear. *Inorg. Chim. Acta*, **251**, 335 (1996).
- [16] Y. Peng, F. Huang, J. Wen, B. Huang, X. Ma, Q. Wang. *J. Coord. Chem.*, **61**, 1503 (2008).
- [17] N. Chebotareva, T. Nyokong. *J. Coord. Chem.*, **46**, 433 (1999).
- [18] M.J.L. Tendero, A. Benito, R. Martínez-Mañez, J. Soto, E. Garcia-España, J.A. Ramirez, M.I. Burguete, S.V. Luis. *J. Chem. Soc., Dalton Trans.*, 2923 (1996).
- [19] R. Ríos, A. Marín, G. Ramirez. *J. Coord. Chem.*, **63**, 1283 (2010).
- [20] J.M. Lloris, R. Martínez-Mañez, J. Soto, T. Pardo. *J. Organomet. Chem.*, **637–639**, 151 (2001).
- [21] A. Koca, A. Kalkan, Z.A. Bayir. *Electrochim. Acta*, **56**, 5513 (2011).
- [22] A. Koca. *Electrochem. Commun.*, **11**, 838 (2009).
- [23] M. Kandaz, M.N. Yarasir, A. Koca. *Inorg. Chim. Acta*, **365**, 256 (2011).
- [24] M. Kandaz, M.N. Yarasir, T. Guney, A. Koca. *J. Porphyrins Phthalocyanines*, **13**, 712 (2009).
- [25] N. Ishikawa, Y. Kaizu. *J. Phys. Chem. A*, **104**, 10 009 (2000).
- [26] M. Matsunami, A. Takaki, H. Maekawa, I. Nishiguchi. *Sci. Technol. Adv. Mater.*, **6**, 172 (2005).
- [27] K.M. Kadish, K.M. Smith, R. Guilard. *The Porphyrin Handbook*, Vol. 11, Academic Press, California, USA (2003).
- [28] M. Kandaz, M.N. Yarasir, B.F. Senkal, A. Koca, B. Salih. *Dyes Pigm.*, **77**, 7 (2008).
- [29] J.A. Duro, T. Torres. *Chem. Ber.*, **126**, 269 (1993).
- [30] B. de Courcy, L.G. Pedersen, O. Parisel, N. Gresh, B. Silvi, J. Pilme, J.-P. Piquemal. *J. Chem. Theory Comput.*, **6**, 1048 (2010).