



# An ionophore–Nafion modified bismuth electrode for the analysis of cadmium(II)

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## ABSTRACT

A novel ionophore–Nafion modified bismuth electrode is described for sensitive and selective anodic stripping analysis of cadmium(II). The electrode is prepared by coating the glassy carbon electrode with the cadmium ionophore *N,N,N',N'*-tetrabutyl-3,6-dioxaoctanedi(thioamide) and Nafion composite. Bismuth is deposited in situ on the electrode surface by plating simultaneously with cadmium in sample solution. Numerous key variables affecting the current response of cadmium have been optimized. The electrode has a linear concentration range of 0.5–10 nM with a deposition time of 180 s. The detection limit is  $1.3 \times 10^{-10}$  M and the relative standard deviations for 0.5 and 7 nM cadmium are 6.5% and 4.5%, respectively. The proposed electrode shows excellent selectivity over other heavy metals, such as copper, lead and indium. The attractive performance of such electrode offers a feasible way to monitor trace cadmium(II) rapidly and precisely in complex matrixes.

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## 1. Introduction

Cadmium is an extremely toxic and carcinogenic metal, which can be easily dissolved and transported by water. The monitoring of cadmium in the environment is a serious concern [1,2]. Among various methods for cadmium determination, anodic stripping analysis offers many advantages over other analytical techniques including high sensitivity, favorable portability, suitability for automation, high speed of analysis, low power requirement, and inexpensive equipment [3]. Bismuth electrodes have been successfully used in anodic stripping analysis since 2000 [4,5] due to their stripping behaviors similar to those of mercury electrodes and the environmentally friendly nature of bismuth. Such electrodes display high sensitivity, well-defined and reproducible response, good resolution, large cathodic potential range and insensitivity to dissolved oxygen. These advantages facilitate the decentralized testing of heavy metals in a wide range of clinical, environmental and industrial applications [6]. To date, many bismuth electrodes have been reported for cadmium analysis [7–9]. However, it should be noted that bismuth electrodes like many other well-established electrodes for stripping voltammetry are subject to interferences from other heavy metal ions, such as

the formation of intermetallic compounds and the peak overlapping problems, which are specific and relate to the nature of stripping measurement [10]. Indeed, coexisting of lead, copper and indium in sample solution can have a significant influence upon the cadmium stripping signal.

Herein, we introduce an ionophore–Nafion modified bismuth electrode for measuring cadmium with high sensitivity and excellent selectivity. Ionophores, commonly used in polymeric membrane ion selective electrodes as ion carriers, are typically macrocyclic molecules with well-defined cavities which have the capability to selectively extract certain ions from an aqueous solution into a lipophilic membrane phase [11]. An ionophore has a definite selectivity toward a specific metal ion due to its complexation specificity, and the relation between the dimensions of the target ion and the ligand site [12]. To supply the stability of the modifying layer of ionophore, Nafion, a sulfonated cation-exchange polymer, can be utilized as the conductive membrane matrix. Although ionophore–Nafion modified electrodes have been employed for stripping voltammetry of heavy metals, the selectivity and sensitivity are still not favorable [13,14]. So far very few ionophore based bismuth electrodes have been reported for determination of trace metals, probably due to the non-conductive property of ionophores [15,16]. In this communication, it will be shown that the ionophore–Nafion modified bismuth film electrode can offer largely improved sensitivity and selectivity for stripping measurement of cadmium.

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## 2. Experimental

### 2.1. Apparatus

All measurements were performed on a CHI 660C electrochemical workstation (Chenhua Instruments, Shanghai, China) with a conventional three electrode configuration. A modified glassy carbon (GC) electrode (3 mm diameter, Chenhua Instruments) was employed as the working electrode, with an Ag/AgCl (3 M KCl) and platinum served as the reference and counter electrodes, respectively. Experiments were performed in a 50 mL polytetrafluoroethylene beaker at room temperature. The micrographs of the modified electrodes were investigated by scanning electron microscopy (SEM, JSM-6700F, operating at 5.0 kV).

### 2.2. Reagents

All solutions were prepared with deionized water (18.2 MΩ cm specific resistance). Metal nitrate salts, alcohol, and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent and of analytical grade purity or better. Sodium hydroxide (99.998%), acetic acid (99.99+%), indium chloride (99.99+%), the cadmium ionophore (*N,N,N',N'*-tetra-butyl-3,6-dioxaoctanedi(thioamide)) and Nafion (5 wt.% mixture of lower aliphatic alcohols and water) were supplied by Sigma Aldrich. To obtain the modification solution, the ionophore (1 mM) and Nafion (1 wt.%) solutions were prepared in THF and alcohol, respectively, and mixed in a 1:1 ratio by volume. 0.1 M acetate buffer of pH 4.5 was prepared with sodium hydroxide and acetic acid as the supporting electrolyte.

### 2.3. Procedures

For fabrication of the ionophore–Nafion modified glassy carbon electrode, 3 μL of the modification solution was transferred onto the well-polished electrode surface. The solvents were left to evaporate at room temperature. The membrane was cured with a hot air stream from a heat-gun for 1 min and left to cool to room temperature [8]. For in situ preparation of the ionophore–Nafion modified bismuth electrode, the ionophore–Nafion modified electrode was immersed into 0.1 M acetate buffer of pH 4.5 containing 1 mg/L Bi(III) and the target metal ion in the presence of dissolved oxygen. The deposition potential of −1.4 V was applied to the ionophore–Nafion modified electrode for 180 s while the solution was stirred. Following the preconcentration step, the stirring was stopped and after 15 s the voltammetry was recorded by applying a square wave voltammetry potential scan with a frequency of 50 Hz, amplitude of 40 mV and a potential step of 4 mV. The scan was applied in the range from −1.4 to −0.3 V. The target metal and bismuth deposited on the electrode surface were removed by electrolysis at 0.3 V for 60 s in fresh supporting electrolyte prior to the next cycle.

## 3. Results and discussion

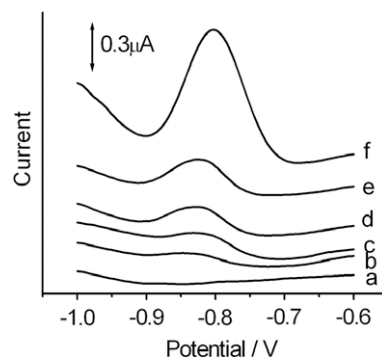
### 3.1. Characterization of the ionophore–Nafion modified bismuth electrode

The morphologies of the ionophore–Nafion layer and ionophore–Nafion/bismuth on the glassy carbon electrodes were characterized by scanning electron microscopy. The ionophore–Nafion layer was found to be a flat and dense coating on the electrode surface. After bismuth deposition, bismuth was coated on ionophore–Nafion layer and some particles were scattered randomly on the electrode surface. To clarify the function of each component in the composite film, the square wave voltammograms recorded

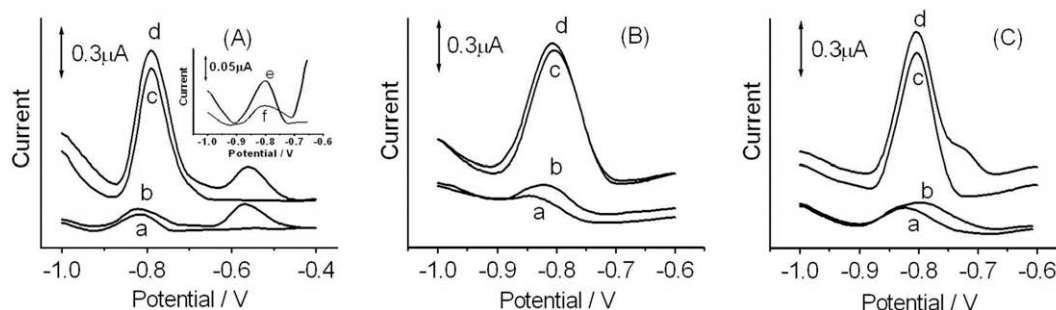
from −1.0 to −0.60 with various electrodes for stripping analysis of cadmium are shown in Fig. 1. No current peak was observed for  $1.0 \times 10^{-8}$  M Cd(II) at bare GC electrode (curve a). Under the same conditions, a very small peak was obtained at Nafion (curve b) or bismuth modified electrode (curve c), which is probably due to the ion-exchange property of the Nafion membrane or the high sensitivity of bismuth material. Larger peaks were found for ionophore–Nafion and Nafion/bismuth modified electrodes, respectively (curves d and e). Ionophore has particular complexing sites for Cd(II) which attract Cd(II) from bulk solution to electrode surface, thus increasing the stripping peak currents. Bismuth can form “fused” or “low-temperature” alloys with heavy metals that facilitate the nucleation processes during accumulation of heavy metal ions and can also increase the stripping peak currents. As shown in Fig. 1, the highest peak occurred at ionophore–Nafion/bismuth modified electrode (curve f). The stripping peak currents at Nafion, bismuth, ionophore–Nafion, Nafion/bismuth and ionophore–Nafion/bismuth modified electrodes are 23, 43, 134, 197, and 753 nA, respectively, indicating that the current response obtained with the ionophore–Nafion/bismuth modified electrode increases remarkably as compared to other electrodes. The enhanced sensitivity might be attributed to the synergistic effect of the ability of ionophore to complex with cadmium, the ion-exchange property of Nafion and the high sensitivity of bismuth material.

### 3.2. Optimization of experimental parameters

Variable experimental conditions affecting the stripping response of the ionophore–Nafion modified bismuth electrode were examined, including the composition of film and deposition parameters. With cadmium concentration of  $3.0 \times 10^{-9}$  M, satisfactory results were obtained with the film containing (in wt.%) 35% ionophore and 65% Nafion. Lower concentrations of ionophore with less functional binding sites may cause insufficient capacity for complexation with cadmium; while higher loadings of ionophore would make the electron transfer difficult due to its non-conductive properties. Deposition potential of −1.4 V was selected as the optimum, since more positive potentials may not be efficient for reduction of cadmium, while more negative potentials could cause hydrogen evolution. The peak current increased with the deposition time until 180 s, and leveled off thereafter due to the saturation of the electrode surface. Hence, 180 s was selected for further experiments.



**Fig. 1.** Square wave stripping voltammetry of (a) bare GC, (b) Nafion, (c) bismuth, (d) ionophore–Nafion, (e) Nafion/bismuth, and (f) ionophore–Nafion/bismuth modified electrodes in acetate buffer containing  $1.0 \times 10^{-8}$  M Cd(II). Deposition for 180 s at −1.4 V; membrane composition (in wt.%): 35% ionophore and 65% Nafion; solutions: 0.1 M acetate buffer (pH 4.5) containing 1 mg/L Bi(III) and  $1.0 \times 10^{-8}$  M Cd(II) in the presence of dissolved oxygen; square wave voltammetry stripping scan with a frequency of 50 Hz, amplitude of 40 mV and a potential step of 4 mV.



**Fig. 2.** Effects of Pb(II) (A), Cu(II) (B), and In(III) (C) on the square wave voltammetry of  $\text{Cd}^{2+}$  at Nafion modified (a, b, e, f) and ionophore–Nafion modified bismuth electrodes (c, d). (A) a, c, e:  $1.0 \times 10^{-8}$  M Cd(II); b:  $1.0 \times 10^{-8}$  M Cd(II) +  $1.0 \times 10^{-8}$  M Pb(II); d:  $1.0 \times 10^{-8}$  M Cd(II) +  $1.0 \times 10^{-6}$  M Pb(II); f:  $1.0 \times 10^{-8}$  M Cd(II) +  $5.0 \times 10^{-7}$  M Pb(II). (B) b, d:  $1.0 \times 10^{-8}$  M Cd(II); a:  $1.0 \times 10^{-8}$  M Cd(II) +  $1.0 \times 10^{-8}$  M Cu(II); c:  $1.0 \times 10^{-8}$  M Cd(II) +  $3.0 \times 10^{-7}$  M Cu(II). (C) a, c:  $1.0 \times 10^{-8}$  M Cd(II); b:  $1.0 \times 10^{-8}$  M Cd(II) +  $1.0 \times 10^{-8}$  M In(III); d:  $1.0 \times 10^{-8}$  M Cd(II) +  $5.0 \times 10^{-7}$  M In(III). Other conditions as in Fig. 1.

### 3.3. Interference study

The stripping analysis of cadmium(II) can be affected by interferences from other heavy metals. In this work, three different metal ions including lead(II), copper(II), and indium(III) were chosen as interfering ions for investigation of the sensor's selectivity. Lead can occupy available deposition and/or coordination sites on the electrode surface and thus decrease the peak current of Cd(II). As shown in Fig. 2A, at Nafion modified bismuth electrode, compared with the stripping peak of  $1.0 \times 10^{-8}$  M Cd(II) alone (curve a), a small peak (curve b) appears at  $-0.58$  V with negligible effect upon the response of Cd(II) when adding Pb(II) at the same concentration of  $1.0 \times 10^{-8}$  M. However, 50-fold excess of lead could cause 50% suppression of the peak current of cadmium (see inset in Fig. 2A, curves e and f). At ionophore–Nafion modified bismuth electrode, the presence of 100-fold excess of lead does not affect the peak current of  $1.0 \times 10^{-8}$  M cadmium at  $-0.80$  V (curve c), although a small peak for lead still can be observed (curve d).

Copper is a more severely interfering metal for cadmium stripping analysis because copper can form intermetallic compounds with cadmium and also compete surface active sites with bismuth. As illustrated in Fig. 2B, at Nafion modified bismuth electrode, the peak signal (curve b) of  $1.0 \times 10^{-8}$  M Cd(II) is suppressed by nearly 40% in the presence of the same concentration of Cu(II) (curve a). However, at ionophore–Nafion modified bismuth electrode, the peak signal is not influenced by even 30-fold excess of Cu(II) (curve c), as compared to the peak current of Cd(II) (curve d).

Indium is another interfering metal since its peak overlaps with that of cadmium. Fig. 2C shows the effects of indium on the peak currents of cadmium at Nafion and ionophore–Nafion modified

bismuth electrodes, respectively. It can be seen that at Nafion modified bismuth electrode, the presence of  $1.0 \times 10^{-8}$  M In(III) can cause the obvious overlapping peaks (curve b) as compared to the stripping peak of Cd(II) alone at the same concentration (curve a). At ionophore–Nafion modified bismuth electrode, 50-fold excess of In(III) can result in a shoulder around  $-0.73$  V (curve d) on the stripping response curve, but does not interfere with the measurement of Cd(II) at  $-0.80$  V (curve c).

### 3.4. Performance of the ionophore–Nafion modified bismuth electrode

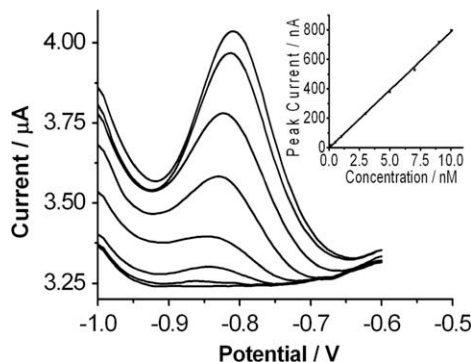
As shown in Fig. 3, the peak current of the proposed electrode is linear with cadmium concentration in the range from 0.5 nM to 10 nM with a sensitivity of 78 nA/nM and a correlation coefficient of 0.9995. The detection limit is  $1.3 \times 10^{-10}$  M ( $3\sigma$ ) with an accumulation time of 180 s. Multiple determinations ( $n = 13$ ) gave relative standard deviations of 6.5% and 5.5% at Cd(II) concentrations of 0.5 and 7 nM, respectively. The detection limit of the present sensor is one order of magnitude lower than those obtained with Nafion modified bismuth film electrodes [8,9]. Such lower detection limit is probably due to the synergistic effect of the ability of ionophore to complex with cadmium, the ion-exchange property of Nafion and the high sensitivity of bismuth material.

## 4. Conclusions

The proposed ionophore–Nafion modified bismuth electrode is suitable for anodic stripping measurement of trace cadmium with high sensitivity and excellent selectivity. Coexisting of 100-fold of lead, 30-fold of copper and 50-fold of indium in sample solution does not cause any interference with the analysis of cadmium. The electrode offers a low detection limit of  $1.3 \times 10^{-10}$  M. Since many ionophores have been developed for use in ion selective electrodes, on-going efforts in our laboratory are aimed at expanding the application of the ionophore–Nafion/bismuth modified electrodes for sensitive and selective stripping analysis of other heavy metals.

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**Fig. 3.** Anodic stripping voltammograms using the ionophore–Nafion modified bismuth electrode for cadmium at different concentrations of 0, 0.5, 1, 3, 5, 7, 9 and 10 nM. Inset shows the calibration curve for cadmium determination. Other conditions as in Fig. 1.

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