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A stannum/bismuth/poly(p-aminobenzene sulfonic acid) film electrode for measurement of Cd(II) using square wave anodic stripping voltammetry

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ABSTRACT

In the present work, a new method for a trace analysis of metal cadmium ion has been developed on the stannum/bismuth/poly(p-aminobenzene sulfonic acid) film electrode in combination with square wave anodic stripping voltammetry. This new electrode was prepared by in situ depositing stannum, bismuth and target metal on the poly(p-aminobenzene sulfonic acid)(p-ABSA) coated glassy carbon electrode. Some key factors including the pH of measure solution, the proper proportion between Bi(III) and Sn(II), the preconcentration time and the preconcentration potential have been studied and optimized. Compared with the traditional bismuth-film electrode, the stannum/bismuth/poly(p-ABSA) film electrode displayed higher stripping current response. In addition, it has the advantages of better stability and less toxicity. Under the optimum conditions, the linear calibration graph for Cd(II) in the concentration range of 0.5–55 $\mu g\,L^{-1}$ was obtained and the detection limit was 0.32 $\mu g\,L^{-1}$. The method was applied to the analysis of cadmium ion in tap water sample with satisfactory results.

1. Introduction

Anodic stripping voltammetry (ASV) has been proved to be a useful and versatile technique for the determination of trace metals in various samples of environmental, clinical, and industrial origin [1]. The first available electrode used to apply ASV was mercury electrodes which include the dropping mercury electrodes, the static mercury electrodes, the hanging mercury electrodes, and mercury film electrodes [2,3]. They factually have advantages in the determination of trace metals due to the wide cathodic potential range and extremely good reproducibility, but as we all know mercury is a kind of high toxic metal.

Bismuth is considered to belong to the less toxic metals and plays less threat to the environment and humans, besides, bismuth-film electrodes (BiFE) have more advantages, for example, simple preparation, high sensitivity, well-defined and undistorted stripping signal, excellent resolution of neighboring peaks, and large cathodic potential range [4,5]. Some recent studies confirm the applicability of BiFE for practical work in environmental trace heavy metal analysis [6–13] and some organic compounds [14–20]. The technique of using BiFE has been proved to be useful for the analysis of heavy metal ions in environment [21,22]. Coverage of bismuth-film electrodes with polymeric membrane can enhance the adherence of bismuth particles with glassy carbon and protect the bismuth surface against adsorption of surface-active compounds and formation of intermetallic compounds, such as the use of Nafion-covered bismuth-film electrode [23–25] and the Bi/poly(aniline) film electrode [26]. In addition, the poly(p-aminobenzene sulfonic acid)(poly(p-ABSA)) modified bismuth-film electrode has been reported [27], in which we created a more stable substrate for practical stripping applications.

In our laboratory, we found that the stannum-film electrode has some characters similar to bismuth-film electrode and have used the stannum-film electrode to detect metal ions for the first time [28,29]. Stannum has less toxicity than bismuth. It provides us a more excellent green electrode material. However, there is no report about the application of the stannum/bismuth-film electrode for the quantification of metal ions.

In the present paper, bismuth and stannum were simultaneously plated into a glassy carbon electrode (GCE) through the poly(p-ABSA) film, resulting in the formation of the Sn/Bi/poly(p-ABSA) film electrode. And the electrode has been applied to detect trace of cadmium ion, which is known to be a hazardous environmental pollutant because of its toxic effects on living organisms [30,31]. The optimization concentration ratio of bismuth and stannum in solution was investigated, and the new electrode material was compared with bismuth film and stannum film. The experimental results indicated that the electrode exhibited more

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excellent response to Cd(II) than alone the bismuth-film electrode or stannum-film electrode.

2. Experimental

2.1. Materials

p-Aminobenzene sulfonic acid (p-ABSA) was purchased from Tian Jing Chemical Plant, China. All chemicals employed in this work were of analytical-reagent grade and used without further purification. All solutions were prepared with doubly distilled water. All the experiments were carried out at room temperature (approximately 25 °C) and without removing oxygen. Solutions of 20 mM p-ABSA, 100 mg L^{-1} Bi(III) and 100 mg L^{-1} Sn(II) were used for the preparation of Sn/Bi/poly(p-ABSA) film electrode. The Cd(II) working solution was obtained by diluting the standard stock solution. 0.10 M Phosphate buffer (pH 7.6) was used as a supporting electrolyte for the poly(p-ABSA) modified electrode. 0.10 M Acetate buffer solutions were prepared by mixing 0.10 M NaAc solution with 0.10 M HAc solution to give the pH required.

2.2. Apparatus

Cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV) were performed with a CHI660B electrochemical station (CHEN HUA Instruments Co., Shanghai, China). A conventional three-electrode system consisted of a glassy carbon working electrode with a diameter of 3.0 mm, a counter electrode made of platinum wire and an Ag/AgCl reference electrode. All electrochemical measurements were carried out in a 10 mL cell. All potentials were given with respect to the Ag/AgCl electrode.

2.3. Measurement procedure

Prior to the deposition of the film, the glassy carbon electrode was polished with water slurry of 0.30 and 0.05 μm alumina powder on a polishing kit to a mirror-like appearance, rinsed and then ultrasonicated with 1:1 (v/v) HNO_3 aqueous solution, absolute ethanol (99.7%) and water, respectively. Then the well-polished glassy carbon electrode was voltammetrically cycled between −0.5 and 1.4 V (vs. Ag/AgCl) at a scan rate of 200 mV s^{-1} in 0.50 M H_2SO_4 for 10 cycles, the activated electrode was placed in 2.00 mM p-ABSA and 0.10 M phosphate buffer solution (pH 7.6) and then it was modified by 15 cycles of potential sweep between −1.0 and 2.0 V (vs. Ag/AgCl) at a scan rate of 200 mV s^{-1}. Subsequently, the modified glassy carbon electrode was voltammetrically cycled and characterized in 0.10 M acetate buffer solution (pH 4.0) until a stable cyclic voltammogram was obtained. After that, the electrode was rinsed with ethanol and doubly distilled water successively, and used for the following experiments.

Stripping voltammetric measurements were performed in a 10 mL electrochemical cell, if not stated otherwise, containing appropriate amounts of Cd(II), 3.0 mg L^{-1} Bi(III), 2.0 mg L^{-1} Sn(II) and 3.0 mL of 0.10 M acetate buffer solution (pH 4.0). The preconcentration was carried out at −1.1 V for 150 s under stirring and after a 10 s equilibration period, the voltammogram was recorded by applying a positive-going square-wave stripping voltammetric potential scan from −1.2 to 0.2 V with a frequency of 35 Hz, pulse amplitude of 75 mV and scan increment of 2 mV. Prior to the next measurement, a 30 s clean step at 0.3 V under stirring was used to remove the residual metals and the stannum/bismuth film. All potentials were referred to the Ag/AgCl reference electrode.

3. Results and discussion

3.1. Electropolymerization of p-ABSA at the GCE surface

Electropolymerization of *p*-ABSA was performed using cyclic voltammetry, which was carried out in the potential range from −1.0 to 2.0 V with a scan rate of 200 mV s^{-1} for 15 cycles in 0.10 M phosphate buffer (pH 7.6) in the presence of 2.0 mM p-ABSA and the voltammograms obtained are shown in Fig. 1. It can be seen from Fig. 1 that in the first scan, two oxidation peaks (a and b) were observed at about 130 mV and 940 mV, respectively. With an increase in the number of cycles, the peaks a and b increased slightly, and a reduction peak, peak c, appeared at a potential of 90 mV, reflecting the continuous growth of the film. The electrochemical polymerization mechanism of p-ABSA at GCE was similar to that reported [32]. After the electrode was dried, a homogeneous brown film was observed on the surface. From these phenomena it can be inferred that p-ABSA was deposited on the surface of GCE by electropolymerization.

3.2. Square-wave voltammetric response of Cd(II) at the Sn/Bi/poly(p-ABSA) film electrode

Square wave voltammograms were recorded at different modified glassy carbon electrodes in a 0.10 M acetate buffer solution (pH 4.0) containing 20 μg L^{-1} cadmium ion. Fig. 2 shows the relevant voltammograms, obtained by square wave anodic stripping voltammetry at the bare glassy carbon electrode (GC) (a), stannum-film electrode (SnFE) (b), bismuth-film electrode (BiFE) (c), Sn/Bi film electrode (d), Sn/poly(p-ABSA) film electrode (e), Bi/poly(p-ABSA) film electrode (f) and Sn/Bi/poly(p-ABSA) film electrode (g). The results exhibited that the peak height of Sn/Bi/poly(p-ABSA) film electrode was obviously enhanced for Cd(II) compared with those of the BiFE, SnFE, Sn/Bi film electrode, Bi/poly(p-ABSA) and Sn/poly(p-ABSA) film electrodes. Therefore, it demonstrated that Sn/Bi poly(p-ABSA) film possesses very attractive electrochemical characteristics with high sensitivity, compared with other four film electrodes.

3.3. Optimization of experimental conditions for determination of Cd(II) at the Sn/Bi/poly(p-ABSA)film electrode

In order to establish the most suitable experimental conditions for the square wave anodic stripping voltammetric measurement of Cd(II) at the modified electrode in acetate buffer solution, a univariate optimization study was performed with the pH of mea-

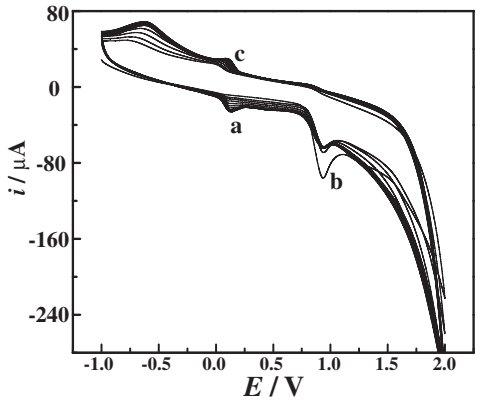

Fig. 1. Voltammograms of the polymerization of p-ABSA. Polymerization conditions: 2.0 mM p-ABSA in 0.10 M phosphate buffer solution (pH 7.6); cycle number: 15; scan rate: 200 mV s^{-1}.