Talanta 88 (2012) 707–710

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Anodic stripping voltammetric measurement of trace cadmium at tin-coated carbon paste electrode

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ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form
20 November 2011
Accepted 22 November 2011
Available online 28 November 2011

Keywords:
Tin film electrode
Carbon paste electrode
Cadmium(II) determination
Stripping analysis

ABSTRACT

A carbon paste electrode modified with tin was used for the determination of trace cadmium by anodic stripping voltammetry. The electroanalytical performance for the determination of Cd(II) on the tin-coated carbon paste electrode(SnF-CPE) was better than that on the carbon paste electrode. The measuring conditions have been optimized. The measurement of trace cadmium on the SnF-CPE has the best response under the conditions of 0.10 mol L^{-1} acetate buffer solution (pH 3.9), 3.5 mg L^{-1} Sn(II), deposition potential of −1.40 V, and deposition time of 150 s. The SnF-CPE revealed highly linear behavior in the concentration range of 2.0–90.0 μg L^{-1} with the detection limit of 1.13 μg L^{-1} for Cd(II). The developed sensor has been applied to the determination of Cd(II) in real water samples with satisfactory results.

1. Introduction

Cadmium is an extremely toxic metal because of its stability in contaminated site and complexity of mechanism in biological toxicity. Once absorbed, cadmium can be accumulated in the body and greatly threatens the health of human. The main organs for cadmium accumulation in humans are kidney, liver, lung and pancreas. Cadmium toxicity may be manifested by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [1]. The development of precise and convenient analytical methods for cadmium determination at trace level is extremely essential because of the high toxicity and potential environmental damage. Electrochemical stripping analysis has been widely used as a powerful tool for measuring trace metals [2–5]. Traditionally, hanging mercury drop electrodes (HMDE) and mercury film electrodes (MFE) have been used as the working electrodes for electrochemical stripping analysis. However, the toxicity of mercury as well as mercury salts and the associated risks of their disposal make the use of mercury electrodes undesirable. In 2000, Wang's research group introduced a new type of electrode, bismuth film electrode (BiFE) [6], which was based on bismuth possessing the same excellent properties as mercury. After that, bismuth electrodes were investigated and showed some properties similar to mercury electrodes [7–11], but with much lower toxicity. In many cases, the BiFEs could offer a more attractive performance compared with the mercury electrodes. Nowadays, BiFEs have been exhibited to take the place of mercury film electrodes successfully [12–18]. Similar to the mercury electrode, BiFEs could be conveniently prepared by plating a thin bismuth film on various substrate materials. To expand the application of BiFEs, some researches about the BiFEs were conducted in our laboratory [19–21]. Although the BiFEs are recognized as a great means in the detection of trace heavy ions, it is known that bismuth also has some toxicity. As we know that tin and bismuth are in diagonal position at periodic table of chemical elements. Therefore, some chemical properties of tin are similar to those of bismuth. In addition, tin also has some unique characters. The ability to form alloys with other metals can be used for the determination of some ions. What is more, tin is an environmental-friendly element and has been used in many fields, such as food processing. Based on the properties of tin mentioned above, our group fabricated the tin film electrodes (SnFEs) based on glassy carbon substrate for the first time, which have already been used for the determination of Cr(III), Cd(II), and Zn(II) [22,23]. Although the carbon paste electrode was widely used because of its inexpensive cost, renewable surface, good stability, and some other excellent properties [24], up to now, there has been no report about the SnFEs used for trace heavy metal detection on the carbon paste substrate.

In this paper, a SnFE on the carbon paste substrate was fabricated for the first time and used for detecting the concentration of Cd(II) by anodic stripping voltammetry. In comparison with the bare carbon paste electrode, the tin film carbon paste electrode (SnF-CPE)

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doi:10.1016/j.talanta.2011.11.070

exhibited superior electroanalytical performance for trace analysis of cadmium combining the environmental-friendly character of tin together with the unique features of the carbon paste electrode.

2. Experimental

2.1. Reagents and chemicals

All chemicals employed in this work were of analytical reagent grade and used as received. Doubly distilled water was used throughout the experiments. An appropriate amount of tin(II) chloride dihydrate purchased from Kelong Chemical Reagent Co. (Chengdu, China) and cadmium chloride purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. (Tianjin, China) were dissolved into doubly distilled water to prepare 100 mg L^{-1} stock solution, respectively. Cd(II) and Sn(II) working solutions were obtained freshly by diluting the corresponding standard stock solutions. Polyethylene rod with a cavity was used as the crust of electrode. Graphite powder and paraffin oil obtained from Chongqing Boyi Chemical Reagent Co., Ltd. (Chongqing, China) were mixed to prepare the carbon paste. Acetate buffer solutions giving the pH required were prepared by step-wise adjustment of 0.10 mol L^{-1} NaAc solutions and 0.10 mol L^{-1} HAc solutions. The test solution was constantly stirred with a small magnetic stirrer.

2.2. Apparatus

Square wave anodic stripping voltammetry (SWASV) was performed with a CHI 660B electrochemical station (Chen Hua Instruments Co., Shanghai, China). A three-electrode system consisted of a tin film carbon paste working electrode with diameter of 3 mm, a saturated Ag/AgCl reference electrode, and an auxiliary electrode made of platinum. All potentials were given with respect to the Ag/AgCl electrode. A pHs-3B pH meter (Dazhong, Shanghai, China) was used for measuring pH. A magnetic stirrer (ca. 300 rpm) was used for convection of the solution during accumulation period. All electrochemical measurements were carried out in a 10 mL cell.

2.3. Procedure

The bare carbon paste electrode (CPE) was prepared by mixing 190.0 mg of graphite powder and 0.04 mL of paraffin oil in a mortar to obtain uniformly wetted paste. A Teflon rod with a cavity (3 mm diameter and 1 mm deep) bored at one end for paste filling was used to construct the body of the carbon paste working electrode and electrical contact to the paste was made with a copper wire through the centre of the rod. A portion of the paste was pressed into the end cavity of the electrode body and leveled off with a spatula. Surface of the carbon paste electrode was manually smoothed by polishing on clean paper before use without any electrochemical pretreatment. In this work, the in situ deposition of tin with the metal ion was carried out. The carbon paste electrode was used after being rubbed on weighing paper in order to get a new surface of the electrode. Then the carbon paste electrode, the reference electrode, and the auxiliary electrode were immersed into a 10 mL electrochemical cell containing appropriate amounts of Cd(II), 3.5 mg L^{-1} Sn(II), and acetate buffer solution (pH 3.9). The in situ deposition potential of −1.40 V was applied to the electrode modified by tin for 150 s under stirring condition. Following the accumulation period, the stirring was stopped and after a 10 s quiescent time without any potential applied to the electrode, the voltammogram was recorded by applying a square wave stripping voltammetric potential scan from −1.20 to 0.20 V.

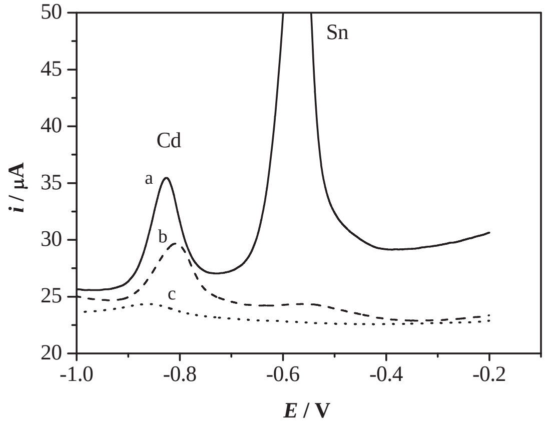

Fig. 1. Square wave anodic stripping voltammetric responses at the SnF-CPE prepared by in situ plating (a), the SnF-CPE prepared by ex situ plating (b), and the bare carbon-paste electrode (c) for Cd(II) in 0.10 mol L^{-1} acetate buffer (pH 3.9). (a) 40.00 μg L^{-1} Cd(II) and 3.50 mg L^{-1} Sn(II); (b) 40.00 μg L^{-1} Cd(II); (c) 40.00 μg L^{-1} Cd(II). (a and c) Deposition potential: −1.4 V; deposition time: 150 s. (b) Step 1: deposition potential: −1.4 V; deposition time: 120 s; 3.50 mg L^{-1} Sn(II). Step 2: deposition potential: −1.4 V; deposition time: 120 s. Scan increment: 4 mV; pulse amplitude: 50 mV; frequency: 25 Hz.

3. Results and discussion

3.1. Anodic stripping voltammetric response of Cd(II) at the SnF-CPE

The square wave anodic stripping voltammetric responses of Cd(II) in a 0.10 mol L^{-1} acetate buffer solution (pH 3.9) containing 40.00 μg L^{-1} Cd(II) at the in situ and ex situ plating tin film carbon paste electrode were investigated, and the results are shown in Fig. 1. The ex situ plating tin film carbon paste electrode was preplated through immersing a carbon paste electrode into a 10 mL of 0.10 mol L^{-1} acetate buffer solution (pH 3.9) containing 3.50 mg L^{-1} Sn(II) with a potential of −1.4 V and a deposition time of 120 s. In addition, square wave anodic stripping voltammetric response of Cd(II) at a bare paste carbon electrode was recorded and the result is also illustrated in Fig. 1. It can be seen from Fig. 1 that although the stripping peaks at both the in situ (curve a) and ex situ (curve b) plating tin film carbon paste electrodes are higher than that (curve c) at the bare carbon paste electrode, the best anodic stripping voltammetric response of Cd(II) can be obtained at the in situ plating tin film carbon paste electrode. Therefore, the further measurements were carried out with the in situ plating tin film carbon paste electrode.

3.2. Effect of pH

The influence of pH on the stripping peak current of Cd(II) was investigated in the pH range of 3.3–4.7 in acetate buffer media and the results are shown in Fig. 2. It can be seen from Fig. 2 that the square wave anodic stripping voltammetric response of Cd(II) increases in the pH range from 3.3 to 3.9 and then decreases. When the pH is too low (<3.9), the decrease in the stripping peak current of Cd(II) can be attributed to the increase of hydrogen generation on the electrode [25]. Nevertheless, at higher pH values, Sn(II) is inclined to hydrolyze [26] and form deposition compounds, resulting in the decrease of the response to Cd(II). Therefore, the acetate buffer solution of pH 3.9 was chosen as the background electrolyte in the following experiments.

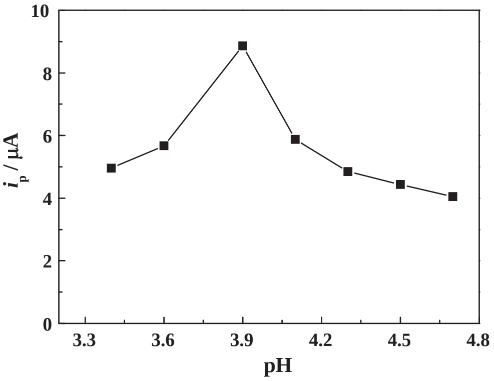

Fig. 2. Effect of pH on the peak current of Cd(II) at the SnF-CPE in the solutions containing 40.00 μg L^{-1} Cd(II), 3.50 mg L^{-1} Sn(II), and 0.10 mol L^{-1} acetate buffer with different pH. Other conditions are the same as in Fig. 1.

3.3. Effect of the tin concentration

The effect of Sn(II) concentration on the peak current of Cd(II) was investigated. 40.00 μg L^{-1} Cd(II) and different Sn(II) concentrations ranging from 0.5 to 4.5 mg L^{-1} in 0.10 mol L^{-1} acetate buffer solution (pH 3.9) were prepared for the determination test, and the results are illustrated in Fig. 3. The response increased initially upon changing the concentration of Sn(II) up to 3.50 mg L^{-1} and started to decrease at higher concentrations. The thickness of tin film had a significant effect on the cadmium stripping signal, which was controlled by the tin solution concentration. When the concentration of Sn(II) was lower than 3.50 mg L^{-1}, it can not form multi-component “fusing” alloys with Cd(II) completely. In contrast, when the concentration of Sn(II) was larger, tin will hold back the target metal and lead to lower peak current [27]. As a result, 3.50 mg L^{-1} was selected as the optimal Sn(II) concentration for the measurements.

3.4. Effect of the deposition potential

The effects of deposition potential on the stripping peak currents of Cd(II) over the potential range from −1.0 to −1.6 V were investigated. The experimental results exhibited the Cd(II) peak current increased in the range of −1.0 to −1.4 V and reached the maximum value at −1.4 V, then decreased gradually. Deposition potential of −1.4 V was selected as the optimum, since more positive potentials may be inefficient for reduction of cadmium, but more negative potentials could cause hydrogen evolution and interfere with the determination of Cd(II) [28]. Therefore, the further measurements were carried out at a deposition potential of −1.4 V.

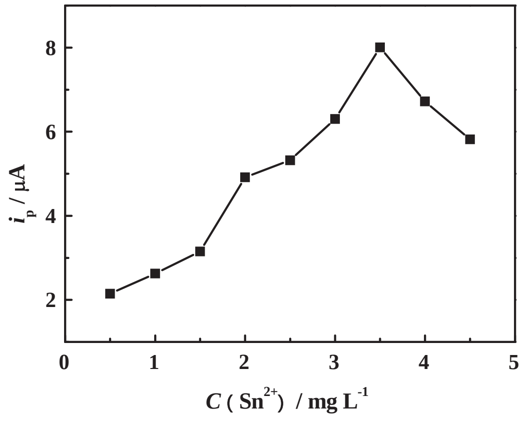

Fig. 3. Effect of the Sn(II) concentration on the stripping peak current of Cd(II) at the SnF-CPE in 0.10 mol L^{-1} acetate buffer (pH 3.9) containing 40.00 μg L^{-1} Cd(II) and different concentrations of Sn(II). Other conditions are the same as in Fig. 1.

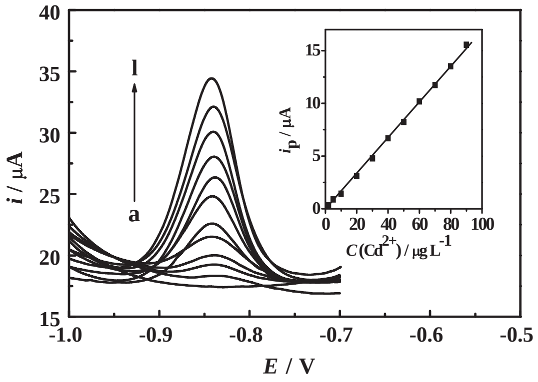

Fig. 4. SWASVs of different Cd(II) concentrations in acetate buffer of pH 3.9. Concentration of Cd(II) (from a to l, μg L^{-1}): 0.0, 2.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0 and 90.0; Sn(II): 3.50 mg L^{-1}; deposition potential: −1.4 V; deposition time: 150 s; other conditions are the same as in Fig. 1.

3.5. Effect of the deposition time and other parameters

Deposition time can apparently influence the determination of Cd(II). The deposition time was studied in the range of 90–240 s for a solution containing 40.00 μg L^{-1} Cd(II). The experimental results exhibited that the peak currents of Cd(II) increased in the first 150 s and then tended to keep constant with further increase of deposition time. Considering that the reproducibility was poor at higher deposition time, the deposition time of 150 s was used as a compromise between high sensitivity and short analysis time. In addition, other parameters of the square wave anodic stripping voltammetry including frequency, scan increment and pulse amplitude were optimized. The best compromise among sensitivity, peak sharpness and background characteristics was obtained at a frequency of 25 Hz, pulse amplitude of 40 mV and scan increment of 4 mV. Thus, these voltammetric conditions were selected for all subsequent analysis.

3.6. Calibration curves and detection limit

To verify the practicality of the SnF-CPE for the determination of Cd(II), the stripping processes of the metal ion were investigated. Under the optimized conditions, the square wave anodic stripping voltammetric responses of different Cd(II) concentrations in 0.10 mol L^{-1} acetate buffer solution (pH 3.9) are shown in Fig. 4. It can be seen from the inset of Fig. 4 that the peak current has a good linear relationship with the concentration of Cd(II). The linear regression equation for Cd(II) is $i_p = 0.1722C - 0.2027$ (i_p: μA, C: μg L^{-1}) in the concentration range from 2.00 to 90.00 μg L^{-1} and the correlation coefficient is 0.9991. The detection limit, defined as the concentration of the analyte giving signals equivalent to three-time the standard deviation of the blank signals (S/N = 3), is 1.13 μg L^{-1}, which is as sensitive as that for Cd(II) in the BiF-CPE [29]. The intra-day precision was tested with six repetitive measurement of 20 μg L^{-1} Cd(II) and relative standard deviation of 3.5% was obtained. The inter-day precision of the proposed method was studied by analyzing 20 μg L^{-1} Cd(II) on three different days and relative standard deviation was 4.7%.

3.7. Interference study

Possible interferences from coexisting trace metal ions and common anions were also tested. The study was carried out by adding

Table 1
<!– no-mfc –>Ratios of interference to 40.0 μg L^{-1} Cd(II)<!– /no-mfc –>.

Foreign substance	Ratio
Ba(II)	800
Ni(II)	3
Cl^-	1200
NO_3^-	2500
SO_4^{2-}	4000
Pb(II)	25
Ca(II)	150
Mg(II)	80
Cr(III)	10
Fe(III)	20
Co(II)	0.5
Cu(II)	0.25

Table 2
Recovery of Cd(II) from the water sample.

Original (μg L^{-1})	Added (μg L^{-1})	Found[a] (μg L^{-1})	Recovery (%)	RSD (%)
ND[b]	10	10.06	100.6	3.3
ND[b]	20	19.45	97.3	2.1
ND[b]	30	30.44	101.5	3.4
ND[b]	40	39.78	99.5	1.8

[a] Mean result of three detections.
[b] Mean of not detected.

various foreign substances which might interfere with the SnF-CPE performance during the measurement of Cd(II) in 0.1 mol L^{-1} acetate buffer solution (pH 3.9) containing 40.0 μg L^{-1} Cd(II) and 3.5 mg L^{-1} Sn(II). The ratios of interference to Cd(II) for a ±5.0% signal change are listed in Table 1. It can be seen from Table 1 that most of ions had little interference for the detection, except for Cu(II) ions. In the presence of high concentration of Cu(II), the stripping peak current of Cd(II) decreases, which is attributed to the fact that Cu(II) can form intermetallic compounds with cadmium and also compete surface active sites with tin [28]. Nevertheless, The copper complex $Cu_2[Fe(CN)_6]$ has a pK_{sp} value of 15.89 and is therefore insoluble. Our experiment result showed that ferrocyanide was the effective masking agent, which could mask copper effectively without having a detrimental effect on the cadmium response. Based on above, the interference of Cu(II) could be alleviated by the addition of ferrocyanide ions [30].

3.8. Analytical application

The sensor was evaluated by carrying out the determination in the water sample taken from the Jialing River. River sample was analyzed after a pretreatment of filtration through a Whatman filter paper. To reduce the interference of Cu(II) and carry out an accurate quantitative determination of Cd(II), the water sample should be treated by the addition of ferrocyanide ions before the determination of Cd(II) concentration. 3.00 mL of the water sample and 1.00 mL of 0.2 mg L^{-1} ferrocyanide ions were pipetted into a 10.00 mL calibrated flask and determined under the optimum conditions. The determination results are listed in Table 2, showing that no Cd(II) was found in the river water sample. In addition, recoveries were examined with given amounts of analyte. Good recovery results are also summarized in Table 2. It is evident that the SnF-CPE can be successfully applied to the determination of Cd(II) in real water samples.

4. Conclusions

The preparation, optimization and practical application of the SnF-CPE which was prepared in situ at the carbon paste substrate electrode are presented. The sensitivity of carbon paste electrode has been improved significantly by the incorporation of metal tin which has less toxicity than bismuth and the detection limit for Cd(II) is as sensitive as that on the BiF-CPE. The SnF-CPE exhibited great stripping voltammetric signals for testing metal Cd(II) ion with a low background over the whole potential range of interest and revealed attractive electroanalytical performance in acidic medium of pH 3.9. Finally, the practical applicability of the proposed electrode was successfully ascertained via measurement of microgram per liter concentration levels of cadmium ions in the real water sample collected from the Jialing River in Chongqing. In addition, our primary experimental result of determination of Cd(II) and Zn(II) at the SnF-CPE indicated this electrode can be used for the simultaneous determination of Cd(II) and Zn(II). Therefore, we infer that the SnF-CPE can also be used for the determination of some other metals.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 20975083), the Municipal Science Foundation of Chongqing City (No. CSTC-2008BB4013), and the 211 Project of Southwest University (the Third Term).

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