Chinese Journal of Chemical Engineering 24 (2016) 410–414

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Energy, Resources and Environmental Technology

Preparation of dendritic bismuth film electrodes and their application for detection of trace Pb (II) and Cd (II)☆

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ARTICLE INFO

Article history:
Received 3 June 2015
Received in revised form 9 July 2015
Accepted 18 July 2015
Available online 14 August 2015

Keywords:
Dendritic Bi film electrode
Electro-deposition
Hydrogen bubble dynamic template
Square wave stripping analysis
Pb(II) and Cd(II)

ABSTRACT

In this paper, dendritic Bi film electrodes with porous structure had successfully been prepared on glassy carbon electrode using a constant current electrolysis method based on hydrogen bubble dynamic templates. The electrode prepared using a large applied current density showed an increased internal electroactive area and a significantly improved electrochemical performance. The analytical utility of the prepared dendritic Bi film electrodes for the determination of Pb (II) and Cd (II) in the range of 5–50 $\mu g \cdot L^{-1}$ were presented in combination with square wave stripping voltammetry in model solution. Compared with non-porous Bi film electrode, the dendritic Bi film electrode exhibited higher sensitivity and lower detection limit. The prepared Bi film electrode with dendritic structure was also successfully applied to real water sample analysis.

1. Introduction

Among the electro-analytical systems, the electrochemical stripping analysis is recognized as a powerful and low cost technique for measuring trace heavy metal ions due to its high sensitivity and selectivity [1–3], especially suitable for on-site analysis of environmental samples. Conventionally, mercury film electrodes were used as working electrodes due to the superior electro-analytical performance of mercury, such as, its wide operational potential window and high overpotential for hydrogen evolution reaction over other materials. However, mercury toxicity and difficulties associated with its handling, storage and disposal cause safety concern [1]. So, researchers have always sought for new electrode materials that can potentially replace toxic mercury in electro-analysis. The bismuth film electrode was introduced as an efficient replacement for mercury counterparts in 2000 [4,5], because Bi is of relatively low toxicity, able to alloy with many metals and has a reasonably wide potential window. The cathodic part of the operational potential window of the bismuth film electrode is very similar to that of mercury. Since then, a lot of research works have been carried out on Bi film electrode preparation and its application [6–17]. Svancara has reviewed recent advance in anodic stripping voltammetry with Bi-modified carbon paste electrodes [18,19]. By now, bismuth based electrodes have been presented in different configurations, that is, bismuth film electrode, bismuth bulk electrode [6–16], and bismuth powder modified carbon paste electrode [17]. These electrodes show a good reproducibility and sensitivity and have been successfully used for measuring various metal ions and other species associated with environmental monitoring. Among these electrodes, Bi film electrode is advantageous. Usually, Bi film electrodes were prepared by *in-situ* or *ex-situ* method with non-porous structure. Recently, it was found that compared to non-porous Bi film electrode, the porous structured Bi film electrodes which are of high surface area and high activity can improve detection performance for the determination of trace heavy metals. This has led to an interest in preparation of micro- and nano-structured electrodes [20–22]. Based on hydrated aluminum oxide template technology, nano-structured Bi film electrode was prepared on a glassy carbon electrode [21]. When the electrode was used for the detection of Pb(II) and Cd(II), the current signals were over 50 times higher than these obtained from a conventional Bi electrode. The polystyrene sphere templates were also used to elaborate highly porous bismuth film electrodes on a gold electrode surface [22]. The porous Bi film with controlled porosity showed an increased internal electroactive area, which led to high sensitivity and low detection limits for Pb(II) and Cd(II) analysis by anodic stripping voltammetry.

Recently, electro-deposition at elevated current density, where hydrogen evolution is pronounced, has been shown to be an effective method to prepare high surface area metals directly (that is, hydrogen bubbles dynamic template technology) and porous Ag, Pt electrodes have been prepared [23,24]. Obviously, the technology can be also used for preparation of porous Bi film electrode.

☆ Supported by the National Natural Science Foundation of China (51472073, 51201058).
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http://dx.doi.org/10.1016/j.cjche.2015.08.012
1004-9541/

The aim of this paper is to prepare Bi film electrodes on glassy carbon electrode surface using constant current electro-deposition with hydrogen bubble dynamic template. The performance of the prepared Bi film for analyzing Pb(II) and Cd(II) by square wave stripping voltammetry was examined.

2. Experimental

All chemicals were of analytical-grade and were used without further purification. All solutions were prepared with ultrapure distilled water. Plating bath consisted of 0.7 mol·L^{-1} $Bi(NO_3)_3$ in 1.5 mol·L^{-1} HNO_3. 0.1 mol·L^{-1} sodium acetate/acetate acid buffer (pH 4.5) served as the supporting electrolyte for Pb(II) and Cd(II) detection.

The Bi film electrodes were prepared on the surface of glassy carbon electrode by constant current electrochemical deposition of Bi from a 0.7 mol·L^{-1} $Bi(NO_3)_3$ in 1.5 mol·L^{-1} HNO_3 in a two-electrode cell at room temperature. Glassy carbon electrode and platinum disc electrode were used as cathode and anode. The H_2 bubbles produced during electroplating Bi were used as dynamic templates. In order to obtain Bi film with different porosity, different current densities were applied for variable time but with the same quantities of electricity. After electro-deposition the electrodes were carefully rinsed by sonic vibration in distilled water for the following measurements.

The electrode surface morphologies were characterized by scanning electron microscope (KYKY2800). The square-wave stripping analysis was performed using the electrochemical workstation (LK3200A, China) in a three-electrode cell. The prepared Bi film electrode was used as working electrode, saturated calomel electrode (SCE) as reference electrode and platinum disc electrode as counter electrode.

The prepared Bi film electrodes were used to analyze Pb(II) and Cd(II) by square wave stripping voltammetry. The analysis process can be divided into three steps. Firstly, the tested solutions containing different contents of Pb(II) and Cd(II) with 0.1 mol/L sodium acetate/acetate acid buffer (pH 4.5) as supporting electrolyte were deoxygenated by purging with pure argon for 30 min [25]; secondly, a certain deposited potential of −1.0 V (*vs.* saturated Hg/Hg_2Cl_2) was applied to the working electrode for some time under stirring in order to convert the heavy metal ions on the Bi film into metal; then stirring was stopped and after 15 s equilibration time, the anodic square-wave stripping votammogram was recorded from −1.0 V to −0.4 V with an amplitude of 20 mV, a frequency of 5 Hz and a potential step of 5 mV. Prior to the next measurement, a cleaning step at −0.4 V for 60 s was performed. Peak currents were registered as analytical signals.

3. Results and Discussion

3.1. Preparation and characterization of the prepared Bi film

The mechanism of formation of the Bi film by hydrogen dynamic template technology has been described in literature [26]. Briefly, at low current density, because of the low nucleation and deposition rate of Bi on glassy electrode surface, non-porous Bi film was obtained. With the increase of deposited current density, the nucleation and deposition rate of Bi on glassy electrode surface were greatly increased, and at the same time, a large number of hydrogen bubbles were evolved and as a result, these hydrogen bubbles played dynamic template roles in the formation of the porous structured Bi film [26].

Bi film electrodes with different structure were obtained by applying a current density of 207, 525 or 605 mA·cm^{-2} for 17.5, 6.9 and 6 s (with electricity quantities equal to 3.6 C·cm^{-2}), which were marked as electrode1, electrode2 and electrode3, respectively. It should be noted that the quantities of electricity is same for Bi electro-deposition, however, current efficiency was different, resulting in different mass of metal Bi. Fig. 1 displays SEM photos of the Bi film surface for electrode1, electrode2 and electrode3, respectively. We can see from Fig. 1 that the cathodic current density is found to have a strong effect on the morphology of Bi film. Along with the increase of the applied current density, the cathode polarization and the speed of hydrogen evolution increase and the obtained Bi film has a higher porosity and ultimately a higher electroactive surface area. When a low current density is applied (electrode1), because the current density is too low to make hydrogen evolution, only Bi^{3+} deposition takes place on the glassy carbon surface and a non-porous Bi film is obtained (Fig. 1(a)). With the increase of current density, besides Bi deposition, hydrogen ion reduction occurs as well, so a Bi film with pores begin to form by attached hydrogen bubbles (Fig. 1(b)) (electrode2). Compared to electrode1, the specific area of electrode2 obviously increases. On further increasing applied current density, because of the increase of hydrogen evolution, very branchy dendrites and small agglomerates of Bi grains are formed on glassy carbon electrode surface (Fig. 1(c)) (electrode3). Obviously, the Bi film electrode is of porous structure. The inset of Fig. 1(c) is the local enlarged image (×5000) from a dendritic structure. We can find from the magnified view in Fig. 1(c) that the single Bi dendrite is assembled by many small dendrites with length of 4–7 μm and width of 2–5 μm. These dendrites with one end tightly grow in the center of the

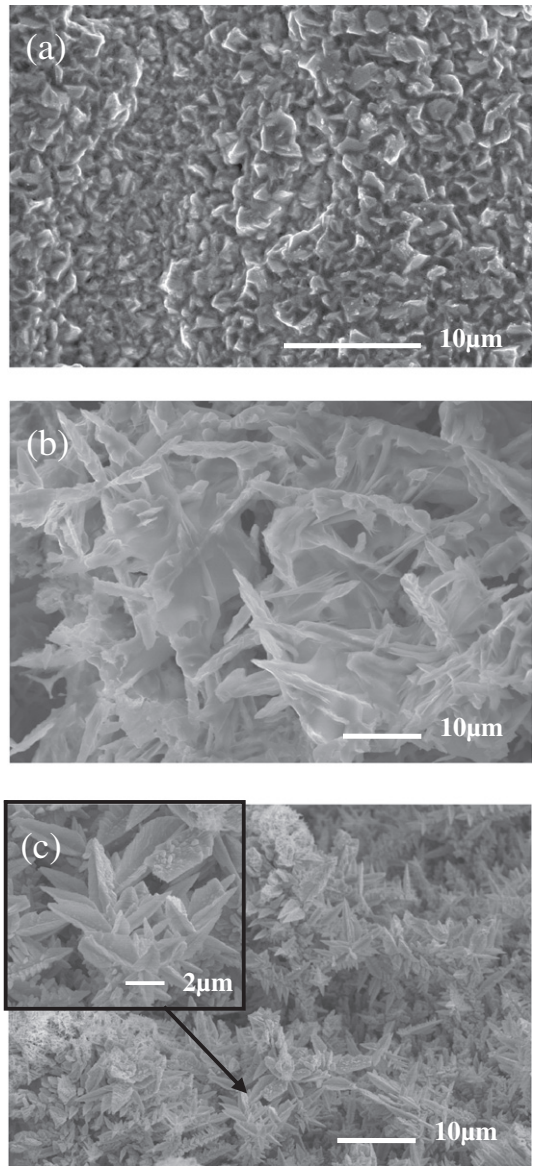

Fig. 1. SEM photos of Bi film electrodes elctrochemically deposited through a H_2 dynamic templates on glassy carbon electrode surface with different deposition current density but same deposition charge of 3.6 C·cm^{-2} (a) 207; (b) 525 and (c) 605 mA·cm^{-2}.