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New application of tin–bismuth alloy for electrochemical determination of cadmium

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ABSTRACT

Electrochemical properties of commercial tin–bismuth alloy were investigated and the tin–bismuth alloy based electrode was used for stripping voltammetric determination of cadmium (Cd^{2+}) for the first time. Electrodeposition and electrochemical stripping of Cd^{2+} on tin–bismuth alloy electrode (SnBiE) were implemented and the results with an excellent linear dynamic range of 5–500 nM, a correlation coefficient of 0.999 and a detection limit of 1.1 nM were obtained under the optimal experimental conditions. It revealed that not only does this environment friendly alloy electrode material have a high hydrogen overvoltage and relatively wide potential window, but also has excellent repeatability and reproducibility. The practical application was carried out for the determination of Cd^{2+} in food samples and the results were consistent well with those by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

1. Introduction

Commercial tin–bismuth (Sn–Bi) alloy is widely used as a potential alternative for Sn–Pb solder in surface mount electronics assembly of welding industry and in the manufacture of all kinds of plastic or rubber mold in manufacturing industry [1,2]. Since J. Wang et al. [3] proposed the bismuth (Bi) as an alternative electrode material to substitute mercury (Hg), there are many applications of the Bi-based electrodes for heavy metals determination due to its low toxicity and similar properties to Hg electrodes [4]. It is well known that the intrinsic properties of electrode materials usually affect the electrochemical performance of the based electrode [5]. Therefore, commercial Sn–Bi alloy with a lamellar eutectic microstructure may meet the growing demands of voltammetric analysis as an alternative electrode material of Hg with low cost, good corrosion resistance and little environmental damage.

Cadmium (Cd) is classified as one of the priority pollutants by the US Environmental Protection Agency due to its wide emission sources and extremely toxic to human beings even in low concentrations [6,7]. It is probably carcinogenic to human by damage human immune and central nervous system and cause serious diseases: renal dysfunction, liver damage, etc. [8,9]. Since the main pathway of Cd entering human body is through daily eating and drinking, monitoring of Cd concentrations in food samples has caught significant attention in many parts of the world, especially those areas where rice is the staple food [10]. Therefore, in this work, Sn–Bi alloy as a novel promising electrode material was used in electrochemical determination of Cd^{2+} in rice samples for the first time. For validation, the results obtained by this proposed Sn–Bi alloy electrode (SnBiE) were comparable to those by ICP-MS.

2. Experimental

2.1. Materials and apparatus

Sn–Bi alloy wires (Sn:Bi, 42:58 wt.%, 1 mm in diameter, purity 99.99%, KAIT Electronic Material Co., Ltd, China) were used as electrode substrates. All electrochemical experiments were performed on a CHI 660D Electrochemical Workstation (CH Instruments, Inc., China) with a conventional three-electrode cell. A SnBiE was employed as the working electrode, with a saturated calomel electrode (SCE) and platinum serving as the reference and counter electrodes, respectively. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was measured with an ELAN DRCII inductive coupling plasma-mass spectrometer (Perkin Elmer Ltd, Hong Kong).

2.2. Preparation of the electrode and analytical procedures

SnBiE was fabricated with Sn–Bi alloy wire (2 cm in length) which was conducted with a copper wire and encapsulated in Teflon. Prior to analysis, the SnBiE was polished on a felt pad with 0.05 μm alumina slurry for a smooth and bright surface. An activated surface of the SnBiE was obtained by cycling the potential from −1.4 to +0.2 V (3 cycles) in 0.1 M acetate buffer solution. Convective electrodeposition of Cd^{2+} was

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carried out at −1.4 V under stirring for 150 s. The stripping voltammogram was then recorded in quiescent solution from −1.4 to +0.2 V after 10 s quiescence time.

3. Results and discussion

3.1. The electrochemical properties of Sn–Bi alloy

The chemical and physical properties of commercial Sn–Bi alloy have been explored, but the electrochemical properties of the Sn–Bi alloy based electrode have not been fully studied so far. Therefore, the application of Sn–Bi alloy in electroanalysis and bio/chemo sensors still needs to be further exploited. The effect of pH values of different electrolytes on the accessible potential windows of the SnBiE is presented in Fig. 1. The applicable potential window of the SnBiE strongly depends on the pH of the electrolyte. At pH 0.96, 3.00, 5.00, 7.96 and 12.88, the potential windows extended from −0.55 to −1.08 V, −0.54 to −1.32 V, −0.62 to −1.44 V, −0.90 to −1.84 V and −0.96 to −1.88 V, respectively. As expected, a limited anodic region (due to the oxidation of tin) but a wide cathodic range (up to −1.88 V) can be observed at the SnBiE. The cathodic limit of the potential window of the SnBiE was extended from −1.08 to −1.88 V with the pH from 0.96 to 12.88, which is mainly depended on the hydrogen evolution reaction. A back-scattered SEM image and the X-ray EDS analysis of the bulk Sn–Bi alloy reported in [1] revealed that this bulk Sn–Bi alloy has a lamellar eutectic microstructure. Therefore, that is presumably due to the special properties of the microstructure to obtain a high hydrogen overvoltage.

The widest useful potential window was recorded in alkaline solution (pH 7.96 and 12.88, curve d and e, respectively). Considering that the target ions are easily hydrolyzed in alkaline solution which may facilitate the oxidation process, deteriorate the electrode and result in an unsatisfactory result, in this work, the determination of Cd^{2+} was then carried out in slightly acid medium.

The stripping voltammograms of SnBiE in 0.1 M acetate buffer solution (pH 5.0) from −1.4 to 0.2 V were shown in Fig. 2. It can be seen that there are a low background current even in the presence of dissolved oxygen and also two stripping signals at the bare electrode which were proved to be the stripping of Sn (−0.650 V) and Bi (−0.094 V), respectively. After addition of 5 μM Cd^{2+} in the solution, an obvious stripping peak of Cd^{2+} was obtained at −0.848 V. It is well known that Bi can form binary or multi-component "fusing" alloy with Cd [4]. Therefore, it can be inferred that the Sn–Bi alloy also forms alloy with Cd, which results in a sensitive response to Cd^{2+}.

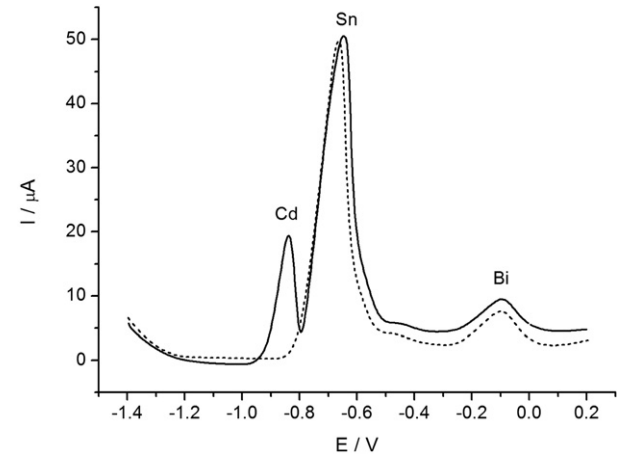

Fig. 2. Stripping voltammograms recorded with the SnBiE surface in blank 0.1 M acetate buffer pH 5.0 with 5 μM Cd^{2+} (solid line) and without Cd^{2+} (dash line).

3.2. Electrochemical determination of Cd^{2+} at the SnBiE

The calibration curve for determination of Cd^{2+} at the SnBiE was established by using differential-pulse anodic stripping voltammetry (Fig. 3). The stripping peak current (i_p) is proportional to the concentration of Cd^{2+} from 5 nM to 0.5 μM ($i_p = 0.035 + 4.86C$, $r = 0.999$, i_p in μA, C in μM) with a sensitivity of 4.86 μA/μM. The detection limit given by the equation $C_L = 3s_{bl}/S$, was calculated to be 1.1 nM, which is lower than that at tin film electrode (SnFE) [11], bismuth film electrode (BiFE) [12], Tantalum electrode [13], and tin/bismuth/poly (p-aminobenzene sulfonic acid) film electrode [14], etc.

Five SnBiEs for 0.5 μM of Cd^{2+} were estimated and the results revealed that the SnBiE had satisfactory reproducibility with a relative standard deviation of 5.4%. Furthermore, to ensure the repeatability of the electrode, a series of 40 repetitive measurements of 0.5 μM Cd^{2+} with a relative standard deviation of 2.4% was obtained. As a new promising electrode with a high repeatability, SnBiE is potentially used in practical analysis.

To demonstrate the performance of the proposed SnBiE in real sample analysis, the contents of Cd^{2+} in rice samples were analyzed

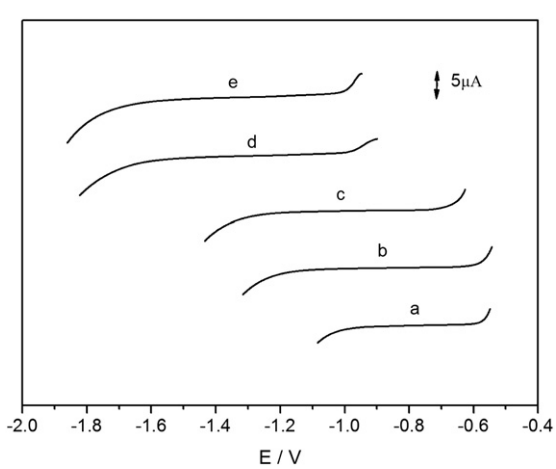

Fig. 1. Accessible potential windows of the SnBiE in different pH solutions: (a) 0.1 M hydrochloric acid, pH 0.96, (b) 0.1 M sodium acetate + 0.1 M hydrochloric acid, pH 3.00, (c) 0.1 M acetate buffer, pH 5.00, (d) 0.1 M sodium acetate, pH 7.96, (e) 0.1 M sodium hydroxide, pH 12.88. Scan rate, 50 mV/s.

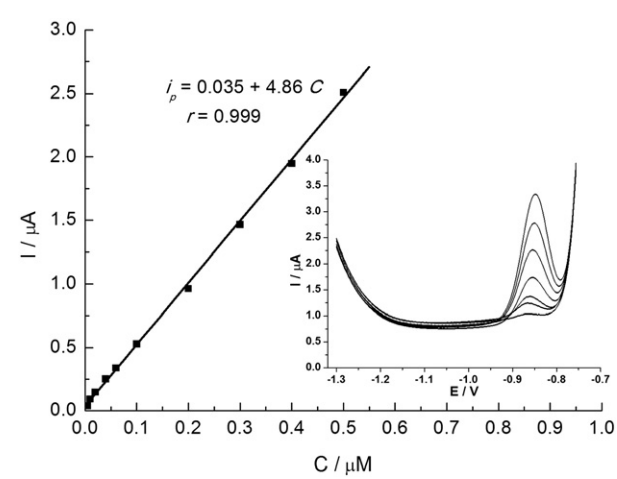

Fig. 3. Calibration curves of Cd^{2+} on the SnBiE. The concentrations of Cd^{2+} for the inset curves are 0.005, 0.06, 0.1, 0.2, 0.3, 0.4, and 0.5 μM from bottom to top, which are in the linear range.

Table 1
Comparison of the SnBiE and ICP-MS for determination of Cd^{2+} in real samples.

Sample	Detected by SnBiE (mg/kg)	Detected by ICP-MS (mg/kg)
Rice sample 1	0.213	0.227
Rice sample 2	0.247	0.250
Rice sample 3	0.047	0.045
Rice sample 4	0.042	0.045
Rice sample 5	0.097	0.099
Rice sample 6	0.091	0.097

by using the standard addition method. In order to illustrate its accuracy in practical analysis, the comparison between the SnBiE and ICP-MS was carried out. As can be seen from Table 1, the results obtained from the SnBiE are in accordance well with those detected by ICP-MS, which indicates the proposed SnBiE can be used directly for accurate analysis of Cd^{2+} in food samples.

4. Conclusions

In this work, new application of solid Sn–Bi alloy based electrode for determination of Cd^{2+} in rice samples by anodic stripping voltammetry was investigated. The Sn–Bi alloy possesses several advantages: besides being an environmental friendly material, it has a high hydrogen overvoltage and relatively wide potential window; moreover, it shows an excellent repeatability and reproducibility. As a new promising electrode, SnBiE has been successfully used in food assays for determination of Cd^{2+}. The high linearity and repeatability revealed that it is potentially used for online and automatic environmental monitoring and construct portable instruments. Meanwhile, many further studies about the properties and applications of this new electrode material are exploiting.

Acknowledgments

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References

[1] Chen SH, Chen CC, Luo Z, Chao CG. Mater Lett 2009;63:1165–8.
[2] Ma G, Zhang H, Zhang H, Li H, Hu Z. Mater Lett 2008;62:1853–5.
[3] Wang J, Lu J, Hocevar SB, Farias PAM, Ogorevc B. Anal Chem 2000;72:3218–22.
[4] Wang J, Lu J, Kirgöz ÜA, Hocevar SB, Ogorevc B. Anal Chim Acta 2001;434:29–34.
[5] Augustin C, Berchmans LJ, Kalai Selvan R. Mater Lett 2004;58:1260–6.
[6] Li J, Guo S, Zhai Y, Wang E. Electrochem Commun 2009;11:1085–8.
[7] Weiss DJ, Rehkdmper M, Schoenberg R, McLaughlin M, Kirby J, Campbell PGC, et al. Environ Sci Technol 2008;42:655–64.
[8] Es'haghi Z, Khalili M, Khazaeifar A, Rounaghi GH. Electrochim Acta 2011;56:3139–46.
[9] Yi H, Mei P. J Appl Electrochem 2008;38:1623–7.
[10] Wen X, Wu P, Chen L, Hou X. Anal Chim Acta 2009;650:33–8.
[11] Czop E, Economou A, Bobrowski A. Electrochim Acta 2010;56:2206–12.
[12] Kefala G, Economou A, Voulgaropoulos A, Sofoniou M. Talanta 2003;61:603–10.
[13] Zhang W, Liu Z, Zhu S, Chen J, Xu G. Electrochem Commun 2010;12:1291–3.
[14] Xiong CH, Luo HQ, Li NB. J Electroanal Chem 2010;651:19–23.