Preparation of a Preplated Bismuth Film on Pt Electrode and its Application for Determination of Trace Aluminum(III) by Adsorptive Stripping Voltammetry

Hongmei Wang,[a] *Zhanglong Yu,*[a] *Zhiliang Wang,*[b] *Haijun Hao,*[a] *Yongmei Chen,**[a] *Pingyu Wan**[a]

[a] Faculty of Science, Beijing University of Chemical Technology, 100029 Beijing, P. R. China
fax: +86-10-64445917; tel: +86-10-64445917
[b] Jiangsu Provincial Academy of Environmental Science, 210029 Nanjing, P. R. China
*e-mail: chenym@mail.buct.edu.cn; pywan@mail.buct.edu.cn

Received: December 17, 2010
Accepted: January 7, 2011

Abstract
Adsorptive stripping voltammetry (AdSV) was successfully explored for the determination of aluminum(III) in sodium carbonate solution (1 M) on a preplated bismuth film electrode (BiFE). Microscopic investigation displays that the morphology of the preplated bismuth film on Pt electrode relates to the plating conditions. The resulted perfect dendritic polycrystalline BiFE demonstrates better performance than the flake single crystal BiFE in AdSV determination of Al(III) in the presence of Eriochrome blue black R (EBBR). Under the selected conditions, the limit of detection(3σ) for Al(III) on flake and dendrite BiFE are 1.02×10^{-8} M and 5.6×10^{-10} M, respectively, and the current variation ratio of the coexistent ions(Ca^{II}, V^{V}, Si^{IV}, Mg^{II}, Fe^{II} and Fe^{III}) is less than $\pm0.700\%$ in all cases.

Keywords: Adsorptive stripping voltammetry, Aluminum(III), Bismuth film electrode, Eriochrome blue black R, Morphology investigation

DOI: 10.1002/elan.201000748

Trace aluminum(III) in concentrated salt solution (for example in 1 M Na_2CO_3 solution) is difficult to determine by inductively coupled plasma-atomic emission spectrum (ICP-AES) [1–3], because the high salinity causes the background value to increase and the sample injector to be blocked. The utilization of direct voltammetric approach for the determination of trace Al(III) in solution is also difficult [4–6] due to the large negative reduction potential of Al(III) which is close to the reduction potential of hydrogen and sodium. An alternative indirect electrochemical strategy for the determination of Al(III) is to monitor the voltammetric response of a complex formed by an electroactive ligand with aluminium [7]. The method of adsorptive stripping voltammetry (AdSV), which has obtained a low detection limit of Al(III) on mercury drop electrode, including the formation and adsorptive accumulation of the complexes, and followed by certain advanced electrochemical measurements of the accumulated analytes [8,9].

Since the year of 2000, bismuth film electrodes (BiFE) have been used to replace mercury electrodes [10–13] in stripping applications due to their large potential window, low toxicity and no need of deoxygenation procedure during measurement. Bi films are usually prepared by ex situ onto the surface of substrate. The resulted bismuth films are usually not homogeneous, and the morphology bismuth films are strongly related with the sensitivity, selectivity and reproducibility of AdSV measurement on it. Several groups' work [14,15] shows that the morphology of the preplated Bi film on different substrates is different. However, it needs more effort to discover the relationship between the morphology of Bi film and the performance of the BiFE [16] since the morphology of Bi film depends on the deposition condition and the nature of the substrate. Herein, we report a well-controlled simple procedure to plate Bi film with polycrystalline or single crystal morphology, and the utilization of the former in the determination of aluminum in concentrated Na_2CO_3 solution by AdSV technique with EBBR as a surface-active ligand.

Preplated bismuth film on Pt electrode: $Bi(NO_3)_3{\cdot}5H_2O$ was used as source of Bi(III) ion for preplating Bi film on Pt electrode. To avoid hydrolysis of Bi(III), HNO_3 was used to acidify the plating solution. KNO_3 was also added to increase the conductivity of the solution. The cyclic voltammogram recorded for the solution containing 1.00×10^{-3} M $Bi(NO_3)_3$ in 0.24 M HNO_3 and1.0 M KNO_3 on Pt electrode show that reductive potential of Bi(III) is $E_{red}=-0.06$ V whereas oxidation potential of Bi(III) is $E_{ox}=0.00$ V.

Theoretically, metallic Bi could be deposited on the surface of Pt electrode only if the applied potential is negative than −0.06 V. However, different kinds of morphology of Bi film were formed if different potentials

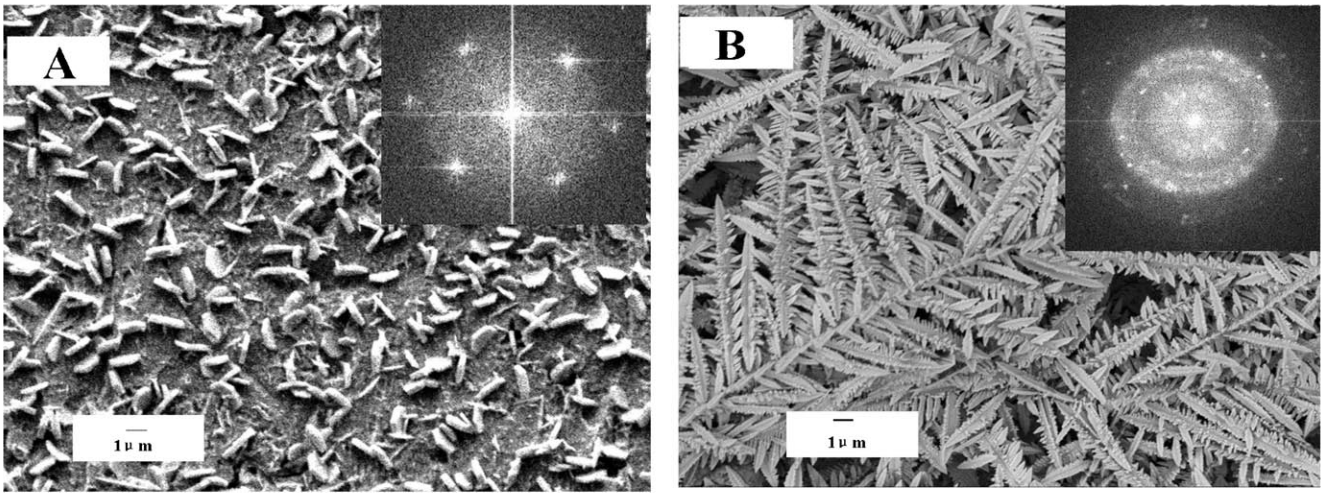

Fig. 1. SEM images and electron diffraction patterns of metallic Bi deposited on Pt electrode in the plating solution of Bi(III) 1.00×10^{-3} M, for 360 s, at plating potential of A) −0.10 V and B) −0.30 V.

were applied. When deposited at less negative potentials, such as −0.10 V or −0.20 V, regular hexagon flake of Bi particles are formed (Figure 1A). The electron diffraction pattern of an isolated flake confirms it is the single crystal of Bi, and when deposited at more negative potential like −0.30 V, the obtained Bi film is continuous dendritic film with much larger surface area than the former one. This dendritic film is polycrystalline demonstrated by electron diffraction pattern.

Except the deposited potential, plating time and the concentration of Bi(III) in the plating solution also affect the morphology of the deposited Bi film. For example, the same perfect dendrite Bi film could also be formed using less concentrated Bi(III) solution but needing more time. However, dendrite Bi film will not be formed when potential is more positive than −0.30 V. That indicates the plating potential is the prerequisitefactor.

The formation of the deposited Bi film on Pt electrode is a process of nucleation and growth of Bi crystallite [17]. The available Bi atoms are yielded from the reduction of Bi(III) on the surface of electrode. The amount of provided Bi atoms in unit time mainly depends on the plating potential. The more negative the plating potential and the more concentrated the Bi(III) solution, the more rapid the Bi atoms are provided. A less feed rate of Bi atoms is favorable for the growth of Bi single crystal, while the polycrystalline is formed when the amount of the available Bi atoms is larger. A very tiny dendrite is obtained at the plating potential below −0.40 V and the concentration of Bi(III) more than 2.00×10^{-3} M, since too fast supply of Bi atoms is beneficial to nucleation instead of crystallite growth.

The two kinds of morphology BiFE obtained in Bi(III) solution of 1.00×10^{-3} M at the plating potential of −0.30 V and −0.10 V respectively, which are composed of single crystal and polycrystallite of Bi (named flake BiFE and dendrite BiFE, respectively), were employed in determination of Al(III) in concentrated Na_2CO_3 solution by AdSV method.

Determination of Al(III) in Na_2CO_3 solution: EBBR was used as a surface-active ligand in AdSV measurement of Al(III). The cyclic voltammograms of an alkaline solution (0.10 M borax buffer solution) containing EBBR (0.01 M) in the presence and absence of Al(III) are shown in Fig. 2. In the absence of Al(III), four anodic peaks are attributed to the oxidation of the free EBBR ligand [8] and no cathodic peak is observed. In the presence of Al(III), one cathodic peak at −0.45 V occurs. This reductive peak is attributed to the reduction of –NH=NH– group in Al-EBBR to $-NH_2$ group. This peak occurs at much more negative potential in free ligand and hardly be observed in a usual potential window, while it shifts to more positive potential in the presence of metal ions (Al(III) in this case)[18], and it is the base of quantitative analysis of Al(III) since the intensity of the peak is monotonically increasing with the amount of Al-EBBR.

As shown in Figure 2 (curve A and B), the intensity of the reductive peaks centered at −0.45 V in the same concentration of Al(III)on dendrite and flake BiFE is different, which means the spontaneous accumulation of the Al-EBBR complex in direct voltammetric measurement is different due to the different morphology of BiFEs. The peak current in the stripping voltammograms following accumulation is enhanced significantly. For example, a 3–5 fold peak enhancement was obtained after 40s' accumulation. Figure 3 shows the dependence of the adsorptive stripping peak current on the accumulation time at two kinds of BiFEs. At both kinds of BiFEs, the peak currents increase as the amount of adsorbed complex increases. The dendrite BiFE gives more sensitive peak than that of the flake one.

The effect of the accumulation potential on the stripping peak current of both BiFEs was examined over the −0.1 to −0.3 V range (the figure is not shown). About 20% increase in the peak was observed on both BiFEs

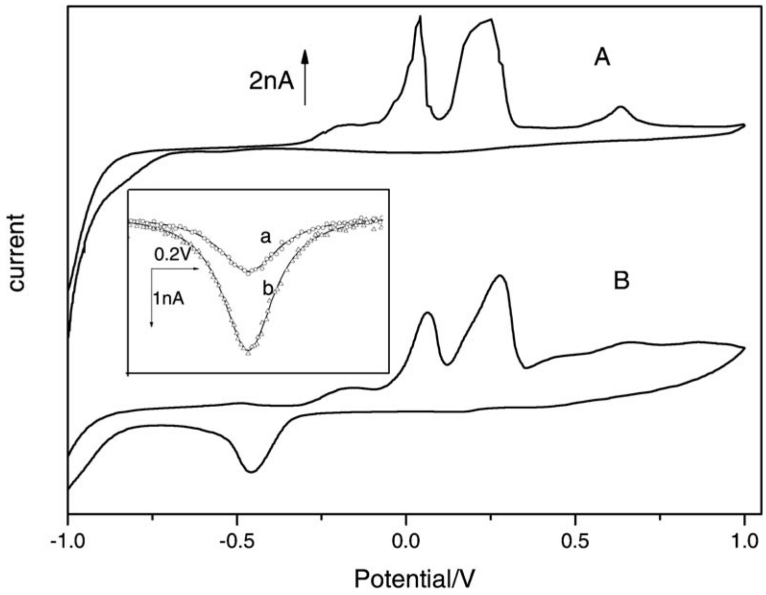

Fig. 2. Cyclic voltammograms of EBBR in 0.10 M borax buffer solution: A) on dendrite BiFE in absent of Al (III); B)on dendrite BiFE in the presence of 7.5×10^{-7} M Al (III). Inset: Different response signals to the same concentration of Al (III): a) on flake BiFE; b) on dendrite BiFE.

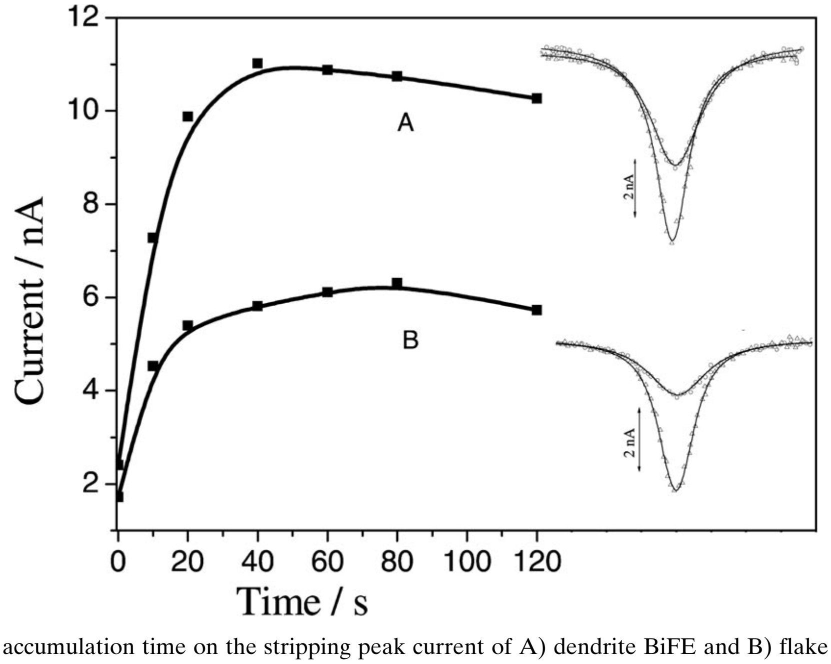

Fig. 3. The effect of the accumulation time on the stripping peak current of A) dendrite BiFE and B) flake BiFE. The parameters of AdSV method: amplitude: 50 mV; step potential: 3 mV; frequency: 15 Hz; accumulation potential: −0.1 V. Inset: Stripping voltammograms in range of −0.55 V to −0.35 V without and with accumulation at −0.1 V for 20 s on both BiFEs.

with accumulations at −0.1 V compared to that of −0.3 V. This can probably be addressed to the rising electrostatic repulsion of the negatively charged amido groups in the Al-EBBR complex.

Figure 4 shows the resulting calibration plots over the stripping peak current and the concentration of Al(III) using standard Al(III) solution under the AdSV method with a step potential of 3 mV, amplitude of 50 mV and frequency of 15 Hz after 40 s accumulation at −0.1 V on both BiFEs. For the dendrite BiFE, the correlation coefficient *R* is 0.9994 over the concentration range of 0.5 to 30 μg L^{-1}(1.8×10^{-8}–1.1×10^{-6} M), the limit of detection is 0.015 μg L^{-1}(5.6×10^{-10} M) of Al(III) at the 3σ level, and the relative standard deviation is 3.80 % at the level of 4 μg L^{-1}(1.50×10^{-7} M for $n=8$). For the flake BiFE, *R* is 0.9989 over the same range, the detection limit of 0.27 μg L^{-1}(1.02×10^{-8} M) and the relative standard deviation of 4.70 %.

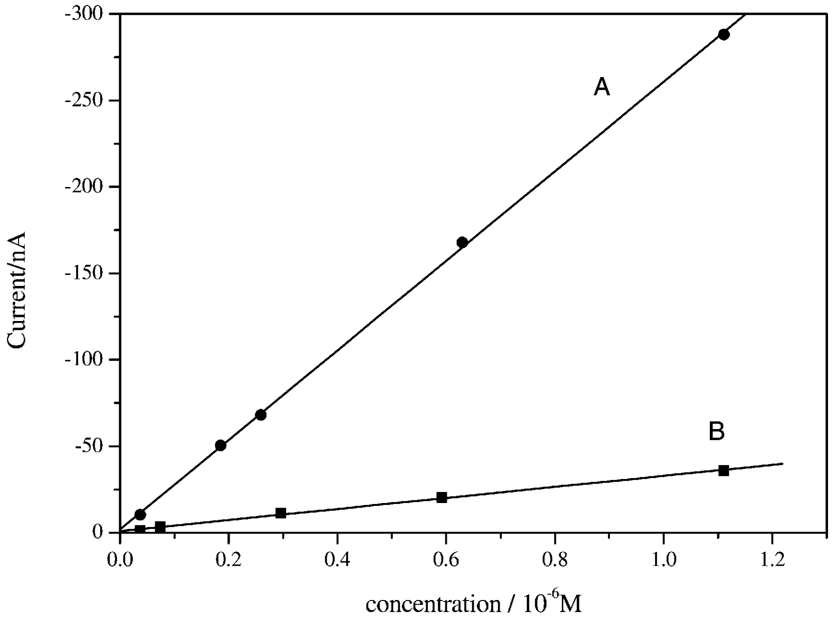

Fig. 4. The calibration curves of AdSV method determining Al(III) on A) the dendrite BiFE and B) the flake BiFE. The parameters of AdSV method as following: step potential of 3 mV, amplitude of 50 mV and frequency of 15 Hz.

Table 1. The interference of coexistent metal ions on the determination results of 2.00 μg L^{-1} Al(III) solution by AdSV method on flake and dendrite BiFE.

	Addition (μg L^{-1})	(η_1) [a] (%)	(η_2) [b] (%)
Ca(II)	6.60	−0.45	−0.66
V(V)	40.00	0.48	0.48
Si(IV)	4.00	0.62	0.42
Mg(II)	0.40	0.04	0.059
Fe(tot)[c]	0.40	0.008	0.007

[a] Current variation ratio on flake BiFE; [b] Current variation ratio on dendrite BiFE; [c] containing Fe(II) and Fe(III).

Table 2. Results for the determination of aluminium in sample by AdSV method on different BiFEs.

Electrode	Al(III) found (μg L^{-1})	Addition of Al(III) calibration solution (μg L^{-1})
Dendrite BiFE	2.29	–
	3.25	1.00
	3.77	1.50
	4.30	2.00
Flake BiFE	2.13	–
	3.10	1.00
	3.61	1.50
	4.17	2.00

A number of metal ions might act as potential interference to determination of Al(III) by AdSV on both flake and dendrite BiFEs were also examined. The results of Al(III) concentration of 1 M Na_2CO_3 solution containing 2.00 μg L^{-1}Al(III) in presence of 3-fold excess of Ca(II), 20-fold excess V(V), 2-fold excess Si(IV), 0.20-fold excess Mg(II) and Fe(II or III) respectively were listed in Table 1. The results show that the current variation ratio due to the coexistent ions is less than $\pm 0.700\%$ in all cases.

A sample of the filtrate after sodium aluminate solution being decomposed by sodium bicarbonate was obtained from the factory. The main solute of the sample is Na_2CO_3, and still containing trace metal ions such as Al(III), Fe(II or III), Ca(II), Mg(II) et.al. The concentration of Al(III) in the sample was determined by AdSV method on both of dendrite and flake BiFEs. The results were listed on Table 2.

The recovery on both BiFEs are among 80%–110%, indicating that the AdSV method provides an efficient and versatile alternative approach to determine trace Al(III) even in concentrated salt solutions. Moreover, the dendrite BiFE demonstrates more excellent performance than the flake one because of the great surface area and good interconnection among the Bi film.

In conclusions, a simple approach to either the single crystal or polycrystalline of preplated Bi film on the surface of Pt electrode could be controlled through adjusting the plating conditions. The resulted BiFEs are applied to determine Al(III) in Na_2CO_3 solution by AdSV method in the presence of EBBR. The polycrystallite BiFE which has dendrite morphology offers more sensitive stripping current than the single crystal one because it is continuous and has larger specific surface area. Both readiness and accuracy of this newly established BiFE are satisfiable for extended uses.

Experimental

Deposition of the bismuth film: The Pt disk electrode (∅ = 3 mm) was polished with alumina slurry (1 μm) followed by ultrasonic washing in triply distilled water. Then the electrode underwent cyclic voltammetry scan in 1 M H_2SO_4 in the range from −0.30 to 1.50 V until the peaks of hydrogen and oxygen emerged respectively, proving that the Pt electrode surface was cleaned and activated. All potentials in this paper are based on SCE. The cleaned Pt electrode was submerged in the deposition solution which containing 1 M KNO_3 and 0.24 M HNO_3 plus $Bi(NO_3)_3$ of various concentrations: 0, 5.00×10^{-4}, 8.00×10^{-4}, 1.00×10^{-3}, 1.20×10^{-3} and 1.60×10^{-3} M, respectively. The deposition potential was controlled at −0.10, −0.20, −0.30 and −0.40 V respectively for 120–360 s with a PARSTAT 2273 electrochemical station (USA) to obtain the BiFE. The morphology of the deposited Bi film was observed with a Jeol JSM–4700LV scanning electron microscope (SEM) and a HITACHI H-800 transmission electron microscope (TEM).

AdSV detection of aluminum on a BiFE: Certain volume of the calibrated solution of Al(III) in Na_2CO_3 solution (1 M) was added to 10.0 ml of 0.10 M borax buffer solution containing 0.50 M KCl and 1.00×10^{-2} M Eriochrome blue black R (EBBR), then diluted to 50.0 mL. The three-electrode system with a BiFE as the working electrode, a SCE as reference electrode and a platinum electrode (10 mm × 7 mm) as counter electrode was employed to perform AdSV with the PARSTAT 2273. A preconcentration potential of −0.10 V was kept for 40 s under stirring, leading to the adsorption of Al-EBBR complex onto the surface of BiFE. The stirring was then stopped, after 10 s a square-wave voltammogram (SWV) was applied from −0.10 to −0.90 V (using a step potential of 3 mV, amplitude of 50 mV and frequency of 15 Hz). A 10-s ‘cleaning’ period (with stirring at 0.00 V) was employed between successive runs.

Acknowledgements

This work was supported by Special Environmental Research Funds for Public Welfare [Project No. 200809016] and Chinese Universities Scientific Fund (No. JD0907).

References

[1] L. Nancy, N. Dennis, *J. Pharmaceut. Biomed.* **2010**, *52*, 652.

[2] T. Qiang, W. Tiebang, V. Antonucci, *J. Pharmaceut. Biomed.* **201**0, 52, 633.

[3] C. J. Iva, Z. Michaela, S. Ilse, *Microchem. J.* **2007**, *85*, 136.

[4] E. A. Hutton, S. B. Hocevar, B. Ogorevc, M. R. Smyth, *Electrochem. Commun.* **2003**, 5, 765.

[5] M. Morfobos, A. Economou, A. Voulgaropoulos, *Anal. Chim. Acta.* **2004**, *519*, 57.

[6] E. A. Hutton, B. Ogorevc, S. B. Hocevar, M. R. Smyth, *Anal. Chim. Acta.* **2006**, *557*, 57.

[7] K. Nowak, A. Bobrowski, *Anal. Lett.* **2005**, *28*, 1887.

[8] X. Mao, J. Li, Z. H. Yan, P. Gao, *Anal. Chem.* **2005**, *6*, 388.

[9] J. Wang, P. A. M. Faria, M. S. Jawad, *Anal. Chim. Acta* **1985**, *172*, 57.

[10] J. Wang, J. Lu, *Electrochem. Commun.* **2000**, *2*, 390.

[11] J. Wang, R. P. Deo, S. Thongngamdee, B. Ogorevc, *Electroanalysis* **2001**, *13*, 1153.

[12] S. B. Hocevar, J. Wang, R. P. Deo, B. Ogorevc, *Electroanalysis* **2002**, *14*, 112.

[13] E. A. Hutton, S. B. Hocevar, B. Ogorevc, M. R. Smyth, *Electrochem. Commun.* **2003**, *5*, 765.

[14] N. F. Zakharchuk, Kh. Z. Brainina, *Electroanalysis* **1998**, *10*, 379.

[15] K. Mieczyslaw, T. Katarzyna, G. Malgorzata, *Electrochem. Commun.* **2005**, *7*, 1185.

[16] M. S. Luiza Nunes, C. Ronaldo Faria, *Electroanalysis* **2008**, *20*, 2259.

[17] K. Agnieszka, B. Andrzej, *Electrochem. Commun.* **2004**, *6*, 99.

[18] A. Ornella, A. Maurizio, S. Corrado, M. Edoardo, *Electroanalysis* **1999**, *12*, 870.