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Stripping analysis of trace cadmium and lead in edible salts by using the over-oxidized poly-(N-acetylaniline) modified electrode with in-situ deposited bismuth film

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Abstract: The over-oxidized poly-(N-acetylaniline) modified glassy carbon electrode with in-situ deposited bismuth film (Bi/over-oxidized PNAANI/GCE) was employed for simultaneous determination of trace Cd(Ⅱ) and Pb(Ⅱ) in edible salts with square wave anodic stripping voltammetry. Such an over-oxidized PNAANI film possesses excellent cation permselectivity, and can remarkably increase the sensitivity and selectivity of the modified electrode. The in-situ deposited bismuth film was used as an alternative to mercury to improve the preconcentration ability for Cd(Ⅱ) and Pb(Ⅱ). The calibration curves for Cd(Ⅱ) and Pb(Ⅱ) both covered two linear ranges, 0.2～3.0 $\mu g \cdot L^{-1}$ and 3.0～33 $\mu g \cdot L^{-1}$. The detection limits of Cd(Ⅱ) and Pb(Ⅱ) were 0.015 $\mu g \cdot L^{-1}$ and 0.029 $\mu g \cdot L^{-1}$ respectively with a deposition time of 300 s. Moreover, this as-prepared electrode has high stability and anti-interference capability. The proposed method was successfully applied to the determination of cadmium and lead in edible salt samples.

Key words: over-oxidized poly (N-acetylaniline); bismuth film; modified electrode; anodic stripping voltammetry; cadmium; lead

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同位镀铋/过氧化聚乙酰苯胺/玻碳电极溶出伏安法测定食用盐中痕量镉和铅

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摘要: 提出了一种新颖的同位镀铋膜过氧化聚乙酰苯胺修饰的玻碳电极(Bi/over-oxidized PNAANI/GCE)

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方波溶出伏安法(SWASV)同时检测食用盐中 Cd(Ⅱ)和 Pb(Ⅱ)的方法.过氧化聚乙酰苯胺膜具有良好的阳离子选择通透性,大大改善了修饰电极检测重金属时的灵敏度和选择性.同位镀铋膜可以作为汞膜的替代物,用于提高修饰电极对 Cd(Ⅱ)和 Pb(Ⅱ)的富集能力.Cd(Ⅱ)和 Pb(Ⅱ)的分析曲线均覆盖了两个线性范围:0.2～3.0 μg·L^{-1}和 3.0～33 μg·L^{-1},在富集时间为 300 s 时,Cd(Ⅱ)和 Pb(Ⅱ)检测限分别为 0.015 μg·L^{-1}和 0.029 μg·L^{-1}.此外,这种修饰电极还具有很高的稳定性和抗干扰性能.最后,该修饰电极被成功地应用于食用盐样品中 Cd(Ⅱ)和 Pb(Ⅱ)的同时测定.

关键词:过氧化聚乙酰苯胺;铋膜;修饰电极;方波溶出伏安法;镉;铅

0 Introduction

Electrochemical stripping analysis is known as a powerful tool for the detection of trace heavy metals[1]. In stripping analysis, mercury film electrode has been widely used as the working electrode owing to its high reproducibility and sensitivity. However, mercury's toxicity and contamination of the surroundings makes it unfavorable for use as electrode material. Recently, many researches have attempted to introduce mercury-free sensors[2]. Since bismuth-film electrode (BiFE) was first introduced for voltammetric measurements of heavy metals by Wang's group in 2000[3-4], BiFEs have been proposed as an alternative to mercury electrodes in analytical chemistry, because bismuth is considered less toxic and less threatening to the environment and humans. Besides, BiFEs have many other advantages, such as simple preparation, high sensitivity, well-defined and undistorted stripping signal, excellent resolution of neighboring peaks and large cathodic potential range[5]. The attractive and unique behavior of BiFEs is attributed to the formation of bismuth-based low temperature alloys. Bismuth is known to form binary or multi-component alloys with numerous heavy metals, including lead, cadmium, thallium, antimony, indium and gallium, etc. Such behavior facilitates the nucleation process during the deposition of heavy metals[6].

Furthermore, bismuth film electrodes can be further modified by coverage with polymeric layers, such as Nafion-coated bismuth film electrode[7-9], Bi/polyaniline film electrode[10], poly-(p-aminobenzene sulfonic-acid) (poly(p-ABSA)) modified bismuth-film electrode[11] and stannum/bismuth/poly-(p-aminobenzene sulfonic acid) film electrode[12]. The polymeric membrane could enhance the adherence of bismuth particles on electrode surface and minimize the interference coming from surface-active compounds.

Over-oxidized polymers with excellent cation permselectivity have been widely used for detecting neurotransmitters, such as dopamine (DA)[13-14], uric acid (UA)[15] and epinephrine (EP)[16]. However, over-oxidized polymer modified BiFEs have not been reported to date to measure trace heavy metals. In this work, an over-oxidized poly-(N-acetylaniline) modified glassy carbon electrode with in-situ deposited bismuth film (Bi/over-oxidized PNAANI/GCE) was successfully applied to the determination of cadmium and lead in edible salt samples.

1 Experimental

1.1 Reagents

N-acetylaniline, bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), lead nitrate ($Pb(NO_3)_2$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), acetic acid (HAc), sodium acetate (NaAc), nitric acid (HNO_3), perchloric acid ($HClO_4$) were all purchased from Sinopharm (Shanghai, China). Three brands of edible salts were purchased from a local supermarket in Hefei, China. All reagents used were of analytical grade and put to use without any further purification. The Bi(Ⅲ), Pb(Ⅱ) and Cd(Ⅱ) working solutions were obtained by diluting the standard stock solutions (1 000 mg·L^{-1}). 0.05 mol·L^{-1}

acetate buffer (pH4.7) was used as supporting electrolyte. All experiments were carried out at room temperature.

1.2 Apparatus and determination

The image of the scanning electron microscope (SEM) was obtained at JEOI JSM-6700F SEM (JEOI, Japan). The X-ray diffraction (XRD) measurements were obtained conducted on the Philips X Pert PRO SUPER XRD (Philips, Holland). The FT-IR spectra were obtained at Nicolet 6700 (Thermo Fisher Scientific, USA). The electronic paramagnetic resonance (EPR) spectra were obtained on a JES-FA200 electron paramagnetic resonance (JEOL, Japan). The control experiments were performed on the X Series 2 ICP-MS (Thermo Fisher Scientific, USA). All electrochemical measurements were performed on a LK98B Ⅱ electrochemistry workstation (LANLIKE Co. Ltd, China) with a conventional three-electrode system comprising a bare or modified glassy carbon electrode (3 mm in diameter) as working electrode, a saturated calomel electrode (SCE) as reference and platinum wire as counter electrode. Cyclic voltammetry and constant potential electrolysis method were used to prepare the modified electrodes. Square wave anodic stripping voltammetry (SWASV) was employed for determining trace amounts of Cd and Pb.

1.3 Electrode preparation

Before use, the glassy carbon electrode was polished to a mirror-like surface with water slurry of 0.05 and 0.03 μm (diameter) α-alumina powder in sequence. Then the electrode was successively ultrasonicated in deionized water and ethanol for 5 min, respectively. Finally, it was dried under nitrogen atmosphere.

The over-oxidized poly-(N-acetylaniline) modified glassy carbon electrode was prepared by cyclic voltammetry/constant potential electrolysis method. Firstly, the prepared bare glassy carbon electrode was polarized at 1.0 V (vs. SCE) in 1 mol·L^{-1} $HClO_4$ solution for 300 s. At high positive potential, a lot of oxygen-containing groups were produced on the surface of glassy carbon electrode, which could improve the stability and adhesiveness of the modified polymer layer. Then the poly-(N-acetylaniline) modified glassy carbon (PNAANI/GCE) was prepared by cyclic potential scanning from −0.2 to 0.90 V in 1 mol·L^{-1} $HClO_4$ solution containing 0.1 mol·L^{-1} N-acetylaniline at the scan rate of 60 mV·s^{-1} for 6 cycles. Lastly, the over-oxidized PNAANI/GCE was obtained by oxidizing PNAANI/GCE at 1.5 V (vs. SCE) in 1 mol·L^{-1} $HClO_4$ for 500 s. After modification, the electrode was thoroughly rinsed with deionized water and kept at room temperature for further use.

1.4 Sample preparation

2.000 0 g edible salt was dissolved in 20 mL 0.05 mol·L^{-1} acetate buffer (pH4.7), and then the solution was quantitatively transferred to a 100.00 mL volumetric flask. 20.00 mL sample solution was taken for measurement of Cd(Ⅱ) and Pb(Ⅱ) by standard addition method.

2 Results and discussion

2.1 Electrochemical and physical characterization of the modified electrodes

The SEM images of PNAANI/GCE and over-oxidized PNAANI/GCE were shown in Fig. 1. It can be seen that the electrodeposited poly-(N-acetylaniline) film (Fig. 1(a)) revealed a nanoporous matrix consisting of a stack of ball-shaped nanoparticles with a diameter of 70 ~ 110 nm. After over-oxidation, remarkable change was observed (Fig. 1 (b)), the ball-shaped nanoparticles were replaced by irregular cube nanoparticles with a size of 100 ~ 200 nm. As we know, the surface energy of a cube is higher than that of a sphere, which could effectively increase the active sites on the modified electrode surface, leading to remarkably improved sensitivity.

It can be seen from XRD spectra (Fig. 1(c)) that poly-(N-acetylaniline) and over-oxidized poly-(N-acetylaniline) were of completely different

crystal structures, which might be the cause of the above-mentioned morphological change. What's more, over-oxidized poly-(*N*-acetylaniline) with larger crystal faces than poly-(*N*-acetylaniline), could effectively increase the active surface of the modified electrode.

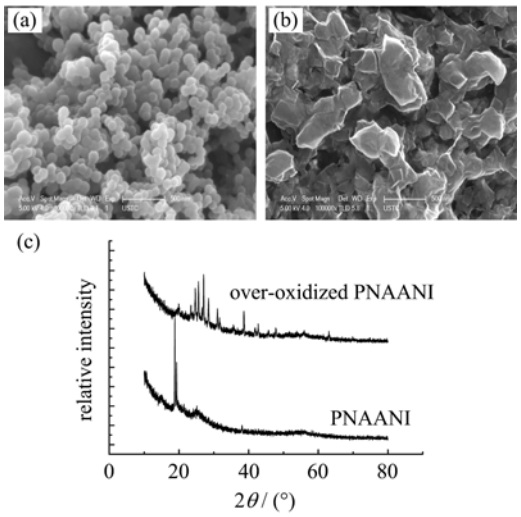


Fig. 1 SEM images of PNAANI/GCE (a) and over-oxidized PNAANI/GCE (b), and XRD (c) patterns of PNAANI and over-oxidized PNAANI

The FT-IR spectra of poly-(*N*-acetylaniline) and over-oxidized poly-(*N*-acetylaniline) were shown in Fig. 2(a). In both cases, the absorption peaks at 1 554 and 1 469 cm^{-1} were due to the stretching of benzenoid and quinoid structures, respectively. The strong peak at 1 298 cm^{-1} corresponded to aromatic C—N stretching. The stretching vibration peaks of N—H and C═O were found at 3 439 and 1 608 cm^{-1}, respectively, and the peak at 794 cm^{-1} could be attributed to the C—H out-plane bending vibration. The peak at 1 117 cm^{-1} was due to the C—H in-plane deformation, which was used to evaluate the electron delocalization in polymers[17]. In PNAANI, the relative intensity of C—H in-plane deformation and stretching vibration peaks of N—H was 3.16, while in over-oxidized poly-(*N*-acetylaniline), it was 1.48, suggesting that the π-conjugated structure of the poly-(*N*-acetylaniline) was lost through over-oxidation, resulting in the decrease in electron delocalization extent and the generation of a large number of anion radicals.

To further prove the generation of a large number of anion radicals by over-oxidation, the electron paramagnetic resonance (EPR) of poly-(*N*-acetylaniline) and over-oxidized poly-(*N*-acetylaniline) were performed, as shown in Fig. 2 (b). The g factors were 1.997 2 for poly-(*N*-acetylaniline) and 1.983 0 for over-oxidized poly-(*N*-acetylaniline), approximate to the 2.002 3 for free electrons, indicating that there were anion radicals in both poly-(*N*-acetylaniline) and over-oxidized poly-(*N*-acetylaniline). Besides, the absorption intensity per unit of mass for over-oxidized poly-(*N*-acetylaniline) was 513, considerably larger than 244 for poly-(*N*-acetylaniline), which shows clearly that more anion radicals were produced after over-oxidation, making positively charged poly-(*N*-acetylaniline), due to the protonation in acid medium, into negative charged over-oxidized poly-(*N*-acetylaniline), resulting in its excellent cation

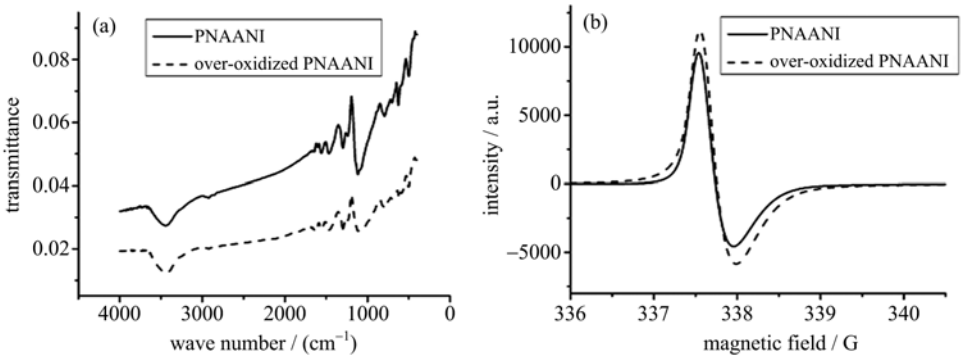
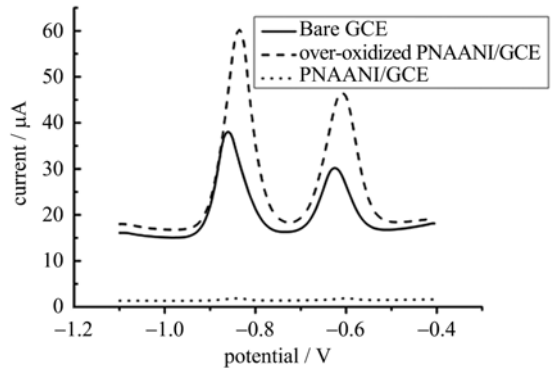


Fig. 2 FT-IR (a) and EPR (b) spectra of PNAANI and over-oxidized PNAANI

permselectivity.

Fig. 3 shows the stripping performance of 30 $\mu g \cdot L^{-1}$ Cd(Ⅱ) and Pb(Ⅱ) at GCE, PNAANI/GCE and over-oxidized PNAANI/GCE. Compared with bare GCE, the stripping peaks at over-oxidized PNAANI/GCE were improved about 90% for Cd(Ⅱ) and 105% for Pb(Ⅱ), respectively. While the stripping signals of target metals at PNAANI/GCE were very small. This phenomenon can be attributed to the positive electricity of poly-(N-acetylaniline) and negative electricity of over-oxidized PNAANI. In addition, the permeability of over-oxidized poly-(N-acetylaniline) is better than that of poly-(N-acetylaniline), so over-oxidized PNAANI/GCE has higher sensitivity than PNAANI/GCE.



Deposition for 120 s at −1.1 V, cleaning for 40 s at +0.4 V, square wave frequency: 10 Hz, amplitude: 50 mV and potential step: 5 mV

Fig. 3　Square wave stripping voltammograms of 30 μg · L^{-1} Cd(Ⅱ) and Pb(Ⅱ) at in-situ deposited Bi film on bare GCE, PNAANI/GCE and over-oxidized PNAANI/GCE in 0.05 mol · L^{-1} acetate buffer (pH4.7) containing 120 μg · L^{-1} Bi(Ⅲ)

2.2　Optimization of experimental conditions

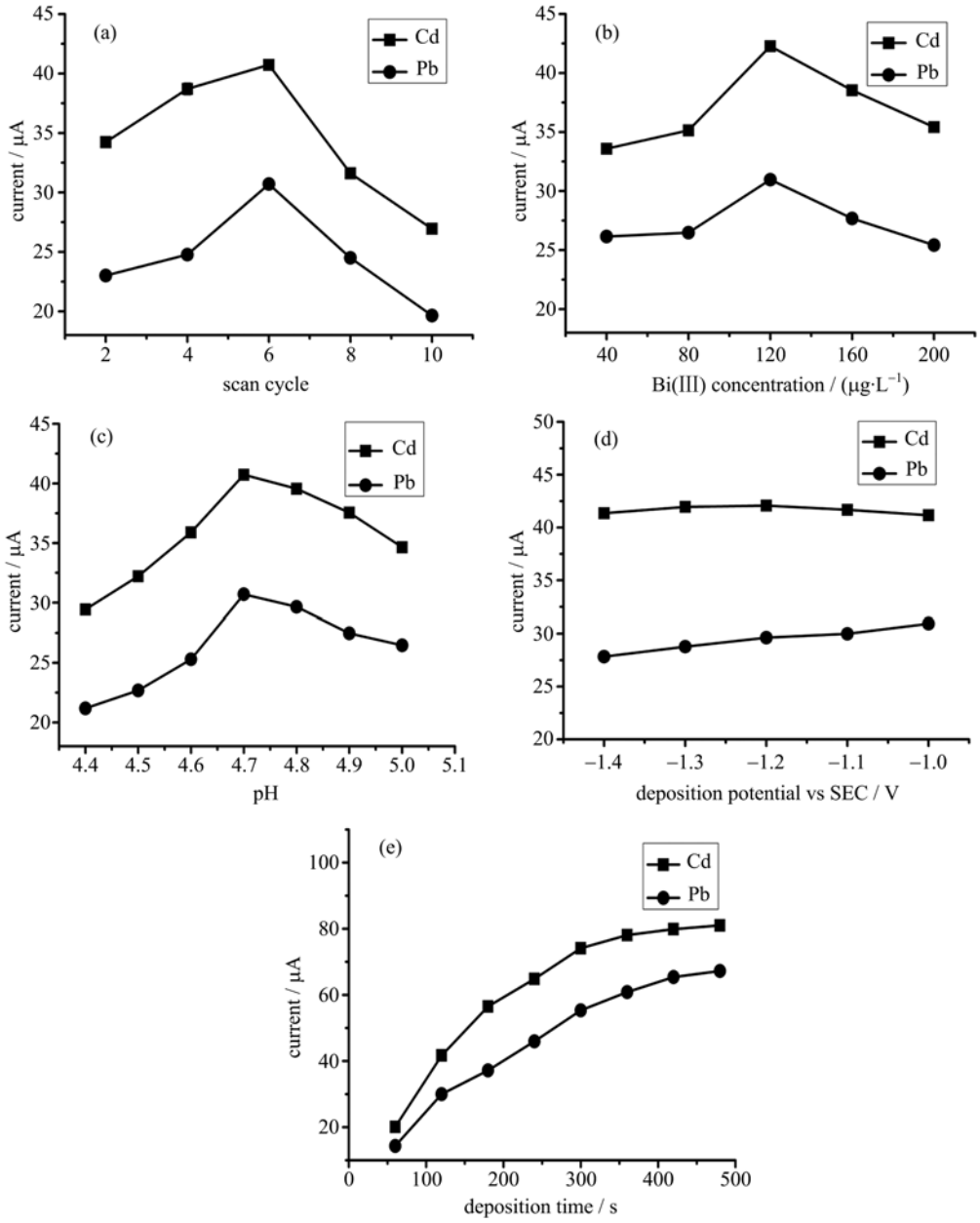
The potential scan cycles for the preparation of poly-(N-acetylaniline) film have an obvious effect on the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ) at over-oxidized PNAANI/GCE, and the results are shown in Fig. 4(a). It can be seen that the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ) increased with the scan cycles increasing from 2 to 6 cycles. While the scan cycles further increased, the stripping signals sharply decreased due to the mass transfer resistance of the thicker polymer layer. Therefore, the electrodeposition for the preparation of poly-(N-acetylaniline) film was carried out with 6 cyclic scans in the follow-on test.

The effect of Bi(Ⅲ) concentration on the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ) is depicted in Fig. 4(b). The thickness of in-situ plated Bi film was controlled by the concentration of Bi(Ⅲ) and the deposition time. When the concentration of Bi(Ⅲ) was below 120 $\mu g \cdot L^{-1}$, the peak heights of Cd(Ⅱ) and Pb(Ⅱ) increased with increasing Bi(Ⅲ) concentration. While the Bi(Ⅲ) concentration was higher than 120 $\mu g \cdot L^{-1}$, the stripping peak currents decreased. Thus, the optimal concentration of Bi(Ⅲ) was chosen as 120 $\mu g \cdot L^{-1}$.

The pH value of the buffer solution has a remarkable effect on the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ). It can be seen from Fig. 4(c) that the optimum pH was 4.7. If the acidity was higher or lower than pH4.7, the current responses would decrease.

The effect of deposition potential on the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ) was tested in the potential rang from −1.4 to −1.0 V, and the results are shown in Fig. 4(d). It is demonstrated that the peak current of Pb(Ⅱ) slightly increased as the potential became more positive, while the peak current of Cd(Ⅱ) kept almost unchanged. But if the potential was more positive than −1.0 V, the stripping peak of Cd(Ⅱ) would not appear completely. Therefore, the deposition potential was chosen as −1.1 V.

The effect of deposition time on the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ) was studied, as shown in Fig. 4(e). The current responses increased as the deposition time increased. Considering the suitable sensitivity and shortening detection time, the deposition time of 120 s was selected for the solutions with higher Cd(Ⅱ) and Pb(Ⅱ) concentrations and 300 s was selected for the solutions with lower Cd(Ⅱ) and Pb(Ⅱ)



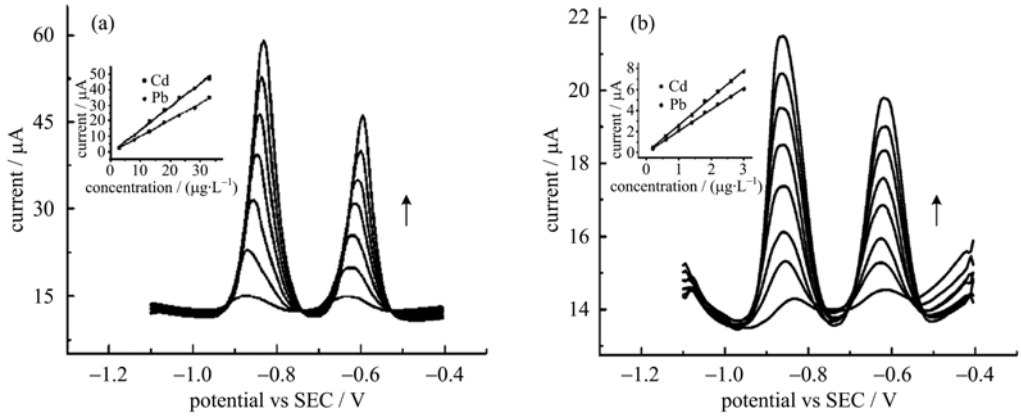
Cleaning for 40 s at +0.4 V, square wave frequency: 10 Hz, amplitude: 50 mV and potential step: 5 mV

Fig. 4 Effect of potential cyclic scans of PNAANI (a), Bi(Ⅲ) concentrations (b), pH value of the electrolyte (c), deposition potential (d) and deposition time (e) on the stripping peak currents of 30 μg · L^{-1} Cd(Ⅱ) and Pb(Ⅱ) at in-situ deposited Bi film on the as-prepared modified electrode in 0.05 mol · L^{-1} acetate buffer (pH4.7)

concentrations.

2.3 Analytical performance

Under the optimized conditions, the in-situ deposited Bi film on over-oxidized PNAANI/GCE was successively used for the simultaneous determination of Cd(Ⅱ) and Pb(Ⅱ) by square wave anodic stripping voltammetry (SWASV). As illustrated in Fig. 5 and Tab. 1, the calibration curves for Cd(Ⅱ) and Pb(Ⅱ) were obtained in two identical linear ranges, 0.2～3.0 μg · L^{-1} (300 s deposition time) and 3.0～33 μg · L^{-1} (120 s deposition time) with the correlation coefficients higher than 0.998 4. The limits of detection, calculated at a signal - to - noise ratio of 3 with a



Deposition for 120 s at −1.1 V, cleaning for 40 s at +0.4 V, square wave frequency: 10 Hz, amplitude: 50 mV and potential step: 5 mV. The insets depict the corresponding calibration plots

Fig. 5　The stripping voltammograms of Cd (Ⅱ) and Pb (Ⅱ) at 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0 μg·L^{-1}, respectively (a), and 3.0, 8.0, 13, 18, 23, 28, 33 μg·L^{-1}, respectively (b)

Tab. 1　Summary of calibration curves and correlation coefficients

concentration range/(μg·L^{-1})	ion	calibration curve	R
0.2～3.0	Cd(Ⅱ)	i_{Cd}= 0.004+2.610C_{Cd}	0.999 2
	Pb(Ⅱ)	i_{Pb}= 0.005+2.050C_{Pb}	0.999 1
3.0～33	Cd(Ⅱ)	i_{Cd}=−1.075+1.506C_{Cd}	0.998 4
	Pb(Ⅱ)	i_{Pb}= −0.694+1.063C_{Pb}	0.999 4

Tab. 2　Comparison of this method for the determination of Cd(Ⅱ) and Pb(Ⅱ) with anodic stripping techniques at Bi film modified electrodes

electrodes description	deposition time/s	detection limited/(μg·L^{-1})		references
		Cd(Ⅱ)	Pb(Ⅱ)	
bismuth film electrode	240	1.0	0.5	[18]
bismuth/carbon paste electrode	300	1.2	0.9	[19]
montmorillonite-bismuth-carbon electrode	120	0.35	0.2	[20]
bismuth film/glassy carbon electrode	300	0.49	0.41	[10]
bismuth/poly(aniline) film electrode	240	1.48	1.03	[21]
Nafion-coated bismuth-film electrodes	600	0.1	0.1	[22]
(Bi/over-oxidized PNAANI/GCE)	300	0.015	0.029	this work

preconcentration time of 300 s, were 0.015 μg·L^{-1} for Cd (Ⅱ) and 0.029 μg·L^{-1} for Pb (Ⅱ), respectively. Furthermore, we have compared this method for the determination of Cd (Ⅱ) and Pb (Ⅱ) with anodic stripping techniques at Bi film modified electrodes and the results are shown in Tab. 2. It can be seen from Tab. 2 that the method proposed has a relatively lower detection limit. The results demonstrate that the proposed in-situ plated Bi film on over-oxidized PNAANI/GCE is sensitive enough for the detection of Cd(Ⅱ) and Pb(Ⅱ) at ppb level, which is promising to be used for analysis of real samples.

2.4　Selectivity and stability

In the stripping analysis of Cd(Ⅱ) and Pb(Ⅱ), interferences may come from the codeposition of foreign ions, which can occupy the active sites supposed to be for target ions on the electrode surface. Tab. 3 shows the changes in stripping peak currents of 30 μg·L^{-1} Cd(Ⅱ) and Pb(Ⅱ) in the presence of Sn (Ⅱ), Hg (Ⅱ), Ni (Ⅱ), Co(Ⅱ), Cr(Ⅲ), Cu(Ⅱ), sodium dodecyl sulfonate

Tab. 3 Interferences of different substances on stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ)

foreign ion	peak current change/%		foreign ion	peak current change/%	
	Cd(Ⅱ)	Pb(Ⅱ)		Cd(Ⅱ)	Pb(Ⅱ)
Sn(Ⅱ)	−2.6	+7.8	Ca(Ⅱ)	−0.3	+0.1
Hg(Ⅱ)	−5.4	+6.3	Al(Ⅲ)	−3.8	−9.5
Ni(Ⅱ)	−3.1	−2.5	Fe(Ⅲ)	+0.01	+2.1
Co(Ⅱ)	+5.8	+8.7	NH_4^+	−1.7	−1.9
Cr(Ⅲ)	−3.3	+3.1	Cl^-	+0.3	+4.9
Cu(Ⅱ)	−98	−100	Br^-	−0.5	−1.4
Triton X-100	+32	+19	F^-	+0.9	+3.2
SDS	−3.6	−2.8	ClO_3^-	−1.6	+2.7
CTAB	−37	−13	BrO_3^-	+0.1	+1.2

(SDS), cetyl trimethyl ammonium bromide (CTAB) and Triton X-100 in the same concentration, and Ca(Ⅱ), Al(Ⅲ), Fe(Ⅲ), NH_4^+, Cl^-, Br^-, F^-, ClO_3^- and BrO_3^- in a 100-fold excess. An error of ±10% was considered tolerable.

BiFEs are prone to be interfered from surface-active compounds that adsorb on the electrode and cause deactivation of its surface[7, 23-26]. In this work, Triton X-100 (a non-ionic surfactant), CTAB (a cationic surfactant) and SDS (a anionic surfactant) were selected as "model" compounds to study the effect of the main surfactants on the stripping response of Cd(Ⅱ) and Pb(Ⅱ) on the in-situ plated Bi film on the over-oxidized PNAANI/GCE. CTAB caused significant suppression to the stripping peak currents of Cd(Ⅱ) and Pb(Ⅱ), due to the electrostatic attraction between CTAB and the negatively charged electrode. On the contrary, the negligible effect of the anionic surfactant SDS is attributed to the electrostatic repulsion between the negatively charged SDS and the modified electrode. Triton X-100 could obviously increase the peak currents of Cd(Ⅱ) and Pb(Ⅱ), which might be attributed to the remarkable sensitization effect of TritonX-100 on the stripping signals[27].

The formation of intermetallic compounds is also considered as a serious interference in the determination of Cd(Ⅱ) and Pb(Ⅱ) by SWASV on BiFEs. From Tab. 3, it can be seen that Cu(Ⅱ) caused remarkable suppression to the peak currents of Cd and Pb, due to the formation of intermetallic compounds. However, this interference can be conveniently and efficiently alleviated by the addition of ferrocyanide ions, which can form a stable complex with Cu(Ⅱ)[18]. In this study, 0.15 mmol · L^{-1} of ferrocyanide was sufficient in eliminating the interference coming from 30 μg · L^{-1} Cu(Ⅱ) on the same concentrations of Cd(Ⅱ) and Pb(Ⅱ). The presence of other ions listed in Tab. 2 did not affect the stripping peaks of Cd(Ⅱ) and Pb(Ⅱ).

The RSDs were obtained 4.6% for Cd(Ⅱ) and 4.7% for Pb(Ⅱ) based on 100 continuous measurements, indicating that the as-prepared modified electrode was of high stability.

2.5 Analysis of edible salt samples

To further demonstrate the practicality of the proposed electrode, it was evaluated by the application in the simultaneous determination of cadmium and lead in edible salt samples with the standard addition method. The contents of Cd(Ⅱ) and Pb(Ⅱ) were detected to be (0.018±0.003) mg · kg^{-1} and (0.18±0.003) mg · kg^{-1}, (0.013±0.002) mg · kg^{-1} and (0.12±0.011) mg · kg^{-1}, (0.014±0.003) mg · kg^{-1} and (0.048±0.004) mg · kg^{-1}, respectively, in three brands of edible salts, which were in good agreement with the results obtained using ICP-MS technique. Besides, good recoveries (90% ~ 108%) were obtained, indicating that the proposed method was precise and reproducible.

Tab. 4　The analytical results of the sample solutions of three brands of edible salts by SWASV and ICP-MS

sample No.	ICP-MS/(μg·L^{-1})		SWASV/(μg·L^{-1})[a]		added/(μg·L^{-1})		found/(μg·L^{-1})		recovery/%	
	Cd(Ⅱ)	Pb(Ⅱ)	Cd(Ⅱ)	Pb(Ⅱ)	Cd(Ⅱ)	Pb(Ⅱ)	Cd(Ⅱ)	Pb(Ⅱ)	Cd(Ⅱ)	Pb(Ⅱ)
1	0.35	3.44	0.35±0.06	3.50±0.05	0.40	10.00	0.73±0.04	13.78±0.70	95	103
					0.80	20.00	1.10±0.08	24.45±0.87	94	105
					1.20	30.00	1.55±0.25	34.74±1.50	100	104
2	0.28	2.54	0.26±0.04	2.31±0.22	0.40	10.00	0.69±0.03	11.51±0.43	108	92
					0.80	20.00	1.12±0.04	21.72±0.41	108	97
					1.20	30.00	1.51±0.17	32.45±1.77	104	100
3	0.31	1.01	0.29±0.06	0.97±0.09	0.40	10.00	0.67±0.03	10.71±0.11	95	97
					0.80	20.00	1.04±0.04	20.98±0.55	94	100
					1.20	30.00	1.37±0.07	31.09±0.98	90	100

【Note】 [a] Value is the mean of three measurements ± confidence interval

3　Conclusion

In summary, a novel method based on in-situ deposited bismuth film on the over-oxidized PNAANI/GCE, for stripping analysis of Cd(Ⅱ) and Pb(Ⅱ) in edible salts has been successfully built. Through over-oxidation, remarkable changes in surface morphology and internal structures of poly-(N-acetylaniline) were found. Such an over-oxidized poly-(N-acetylaniline) film with excellent cation permselectivity, can greatly increase the sensitivity and selectivity of the modified electrode. As a result, the as-prepared electrode demonstrated high sensitivity, good linearity, outstanding selectivity and excellent stability. Furthermore, the proposed method was successfully applied to the determination of Cd(Ⅱ) and Pb(Ⅱ) in edible salt samples. This environmentally friendly in-situ deposited bismuth film on over-oxidized PNAANI/GCE is expected to be employed for analysis of trace heavy metals in foodstuff samples.

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