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# Fabrication of an organic-inorganic hybrid composite bismuth film electrode for stripping analysis of trace Cd(Ⅱ) and Pb(Ⅱ)

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**Abstract**: A novel electrochemical sensor (organic-inorganic hybrid composite bismuth film electrode) was fabricated on a glassy carbon substrate electrode by an electrochemical co-deposition of polyaniline and bismuth followed by plating a thin layer of bismuth on the hybrid film. The hybrid composite bismuth film electrode was applied to detect trace Cd(Ⅱ) and Pb(Ⅱ) in 0.1 mol/L acetate buffer solution (pH 4.7) by square ware anodic stripping voltammetry. The influencing factors of stripping signals and the operational parameters were investigated in detail. The newly developed electrode revealed highly linear behavior in the examined concentration range from 1 to 90 $\mu g \cdot L^{-1}$ for both test metal ions, with the detection limits of 0.2 $\mu g \cdot L^{-1}$ and 0.5 $\mu g \cdot L^{-1}$ for Cd(Ⅱ) and Pb(Ⅱ) respectively, offering good coefficients of variation (CVs) of 4.3% and 6.1% for Cd(Ⅱ) and Pb(Ⅱ) (50 $\mu g \cdot L^{-1}$, $n=50$) respectively. After 30 d, the stripping peak currents for 50 $\mu g \cdot L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ) on the composite film were detected decreasing 3.2% and 4.9%, respectively. The long term stability makes it possible to be applied in on-site monitoring of heavy metals in environmental water.

**Key words**: bismuth; polyaniline; lead; cadmium; anodic stripping voltammetry

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# 有机-无机杂化复合铋膜电极溶出伏安法测痕量镉、铅离子

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**摘要**: 将铋和聚苯胺共沉积在玻碳电极上制备了杂化膜, 然后在杂化膜上沉积一层铋膜, 制备了一种新颖的电化学传感器——有机-无机杂化复合铋膜电极(HCBiFE), 用于痕量重金属离子Cd(Ⅱ)和Pb(Ⅱ)的检测(0.1 mol/L醋酸缓冲溶液, pH 4.7). 优化了镀膜条件、离子测试参数. 在1～90 $\mu g \cdot L^{-1}$的浓度范围内, 两离子溶出峰电流与浓度呈现出良好的线性关系, 富集时间120 s时, Cd(Ⅱ)和Pb(Ⅱ)的检测限分别低至0.2, 0.5 $\mu g \cdot L^{-1}$. 该复合膜具有很好的稳定性和重现性, 能够抗机械剥蚀、不易脱落, 对50 $\mu g \cdot L^{-1}$的

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Cd(Ⅱ)和 Pb(Ⅱ)连续测定 50 次,相对标准偏差分别为 4.3%,6.1%.30 d 后,该复合膜电极对 Cd(Ⅱ)和 Pb(Ⅱ)溶出峰电流分别下降 3.2%,4.9%,表明该复合膜电极性能稳定,有望应用于环境水体的现场监测.

**关键词**:铋;聚苯胺;铅;镉;阳极溶出法

## 0 Introduction

The stripping analysis has long been employed as a powerful tool for detection of trace heavy metals, due to its effective built-in preconcentration step in conjunction with specially modified electrodes[1]. Mercury film electrode (MFE) has been widely applied in stripping analyses during the last six decades because of its excellent reproducibility and high sensitivity[2]. However, owing to its dramatic toxicity and secondary pollution to the environment, mercury has been suggested to be replaced by other materials, such as chemically modified carbon, gold, platinum, silver, iridium, metal alloys and amalgams, etc[3-8]. The bismuth film (BiFE), which was proposed by Wang[9] in 2000, has received considerable attention. Due to its low toxicity, environment-friendly, interference-free of oxygen, wide potential window and excellent electrochemical behavior, the bismuth film is one of the most promising alternatives for mercury electrode[10-11]. But the bismuth film electrode in use is usually affected by machinery eroding, and the bismuth film would gradually shed, making the substrate electrode bare and lose its function. This is the most serious obstacle for long term practical use in on-site monitoring of heavy metals in environmental water.

Polyaniline (PANI)[12-13] is one of the most investigated conducting polymer in electrochemical sensor on account of its low cost, easy preparation, good environmental and chemical stability, and excellent electro-activity. Electrochemical polymerization of the monomer aniline is a simple technique with good reproducibility[14]. Neves et al[15] achieved a net-interlaced structured polyaniline at the surface of the glassy carbon electrode by cyclic voltametry in sulfuric acid medium, which exhibited excellent adhesion and stability.

Herein, the organic-inorganic hybrid composite bismuth film electrode (HCBiFE) is proposed, which was fabricated by plating a thin layer of bismuth potentiostatically on the hybrid bismuth-polyaniline film modified glassy carbon electrode (GCE). The composite bismuth film electrode exhibits an excellent behavior for the stripping analysis of Cd and Pb in 0.1 mol/L acetate buffer solution (pH 4.7) by square ware anodic stripping voltammetry.

## 1 Experimental

### 1.1 Apparatus

All electrochemical experiments were performed on an LK98B Ⅱ electrochemistry workstation (LANLIKE Co. Ltd., Tianjin, China). A three-electrode configuration was employed, consisting of the composite bismuth film modified glassy carbon electrode (2 mm in diameter) as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode as the reference electrode. All measurements were carried out in one-compartment voltammetric cell (20 mL) at room temperature. All glassware was carefully cleaned by being immersed in 3% (mass fraction) $HNO_3$ over 24 h and rinsed thoroughly with double distilled water. Field emission scanning electron microscopy was performed on a JEOL JSM-6700F SEM system to characterize the morphologies of the resulting PANI film, Bi film, Bi/PANI and Bi/Bi-PANI composite film modified glassy carbon electrodes.

### 1.2 Reagents

Aniline, bismuth nitrate pentahydrate ($Bi(NO_3)\cdot 5H_2O$), lead nitrate ($Pb(NO_3)_2$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2\cdot$

$4H_2O$), disodium ethylene diamine tetraacetic acid (EDTA), acetic acid (HAc), sodium acetate (NaAc), nitric acid ($HNO_3$), sulfuric acid ($H_2SO_4$), and hydrochloric acid (HCl) were all purchased from Guoyao Group Co. (Shanghai, China). Standard solutions of Pb(Ⅱ) and Cd(Ⅱ) were obtained by diluting the corresponding stock solutions prepared with $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$, respectively. All chemicals used were of analytical reagent grade and used as received. Unless otherwise stated, all solutions were prepared with double distilled water.

### 1.3 Electrode preparation and modification procedures

In order to avoid contamination by oxidation products and to obtain a clean renewed electrode surface, electrode preparation steps were performed before the usage of the GC electrode in electrochemical experiments: the surface of the GC electrode was mechanically polished with 1.0, 0.3 and 0.05 $\mu$m alumina-water slurry, respectively, using a polishing cloth. To remove impurities, the polished electrode was then sonicated successively in 1 : 1 nitric acid, acetone and double distilled water respectively for 5 min, and dried naturally in air. After that, the Bi-PANI film modified GCE was prepared by cyclic voltametry at a scan rate 0.05 $V \cdot s^{-1}$ for 10 cycles from −0.5 to +0.9 V (vs. SCE), resulting in the organic-inorganic hybrid film of bismuth and polyaniline was deposited on the surface of the pretreated GCE in the plating solution containing 0.005 mol/L aniline, 0.05 mol/L $H_2SO_4$, 0.01 mol/L Bi(Ⅲ), and 0.015 mol/L EDTA. Then a thin layer of bismuth was plated potentiostatically on the prepared Bi-PANI hybrid film modified GCE at the potential of −0.6 V for 240 s under stirring, and the hybrid composite bismuth film modified glassy carbon electrode, Bi/Bi-PANI/GCE, was fabricated.

### 1.4 Square wave anodic stripping analysis of Pb(Ⅱ) and Cd(Ⅱ)

Square wave anodic stripping voltammetry was employed for determination of Pb(Ⅱ) and Cd(Ⅱ) with the Bi/Bi-PANI/GCE as working electrode. 0.1 mol/L acetate buffer solution (pH 4.7) was served as the supporting electrolyte. The instrumental conditions were as follows: deposition potential −1.1 V, equilibration time 15 s, square-wave amplitude 35 mV, square-wave frequency 35 Hz, potential step 5 mV, cleaning potential +0.3 V, and cleaning time 30 s. The cleaning potential was used to remove the target metals on the electrode surface after each measurement.

## 2 Results and discussion

### 2.1 The morphology of the Bi/Bi-PANI composite film

The scanning electronic microscopic (SEM) images of the PANI film, Bi film, Bi/PANI and Bi/Bi-PANI composite film modified GCEs are shown in Fig. 1. Here, the PANI film and Bi film modified GCEs were traditionally prepared by cyclic voltametry and potentiostatic plating, respectively. The net-interlaced structured polyaniline and nano-structured bismuth film are clearly illustrated in Fig. 1(a) and (b). As shown in Fig. 1(c), the crystalline particles of bismuth were filled in the grid meshes of the structured polyaniline and grew uniformly to form nanorods with two tips. This demonstrates that the combination of bismuth particles and polyaniline was chemically hybrid and intimate. In Fig. 1(d), it is also obvious that bismuth nanoparticles were well-distributed on the surface of the hybrid Bi-PANI film and formed plum flower shaped structures while on the bare GCE different shapes and the sizes of bismuth crystalline particles were generated. This particular hybrid composite bismuth film would be beneficial for the deposition of heavy metal ions.

### 2.2 Voltametric responses of Pb(Ⅱ) and Cd(Ⅱ) at the HCBiFE

The square wave stripping voltammograms of Pb(Ⅱ) and Cd(Ⅱ) in 0.1 mol/L acetate buffer

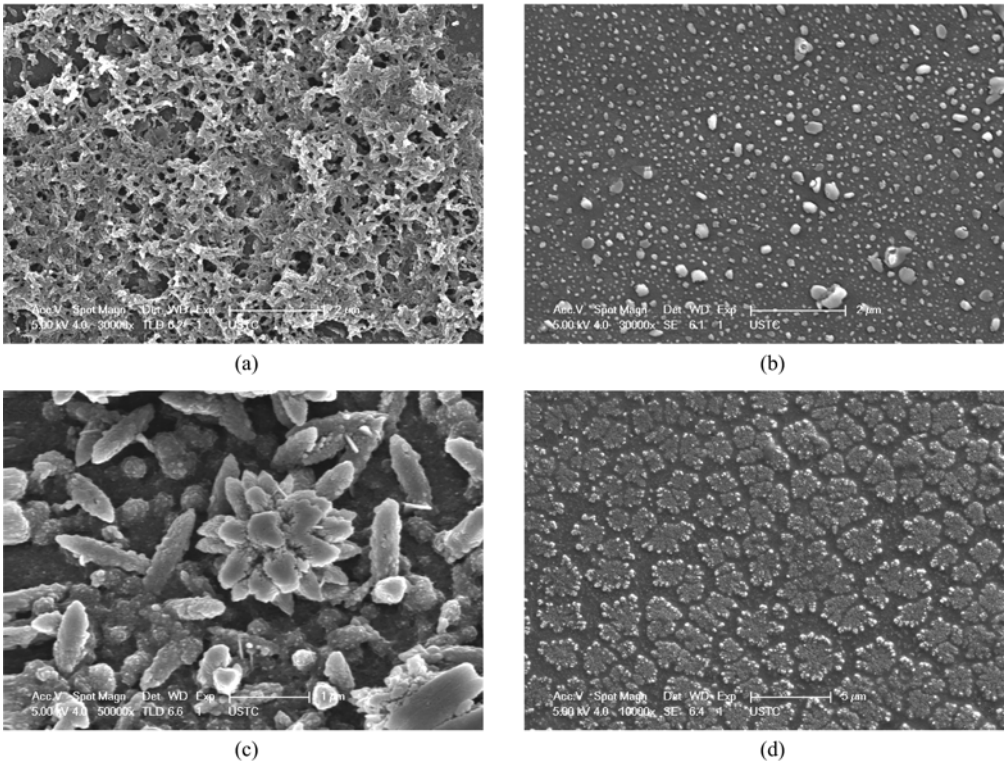



**Fig. 1 SEM images of PANI film (a), Bi film (b), Bi/PANI film (c), and Bi/Bi-PANI composite film (d) modified GCEs**

solution (pH 4.7) at different film electrodes are shown in Fig. 2. Evidently, the Bi/Bi-PANI composite film electrode displayed the highest sensitivity (see Fig. 2(a)) towards detection of Pb(Ⅱ) and Cd(Ⅱ) with sharp, well-defined and favorably separated stripping peaks. In comparison with the Bi-PANI and Bi film electrodes (see Fig. 2(b) and (c)), the stripping peak currents at the HCBiFE increased by about 60% and 166% for lead and 48% and 108% for cadmium, respectively. The superior behavior of HCBiFE could be attributed to three reasons: ① similar to mercury, bismuth could form metal alloys with Pb and Cd, making it easier to reduce Pb(Ⅱ) and Cd(Ⅱ), ② the bismuth nanorods, formed in the polyaniline grid meshes, possess higher electro-activity, which could effectively attract heavy metal ions from the bulk solution to the electrode surface, and ③ the reduced polyaniline, which is electronegative at the deposition potential, facilitates the non-faradaic accumulation of metal cations Pb(Ⅱ) and Cd(Ⅱ).

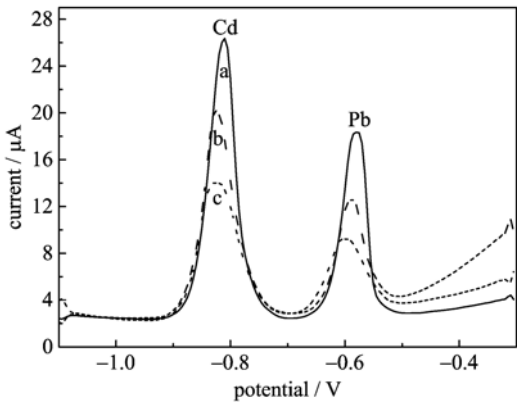
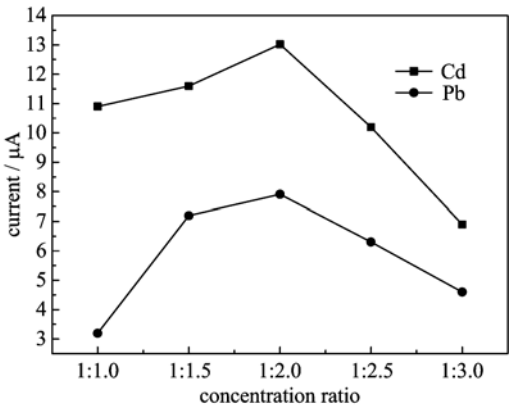



**Fig. 2 Anodic stripping voltammograms of Cd(Ⅱ) and Pb(Ⅱ) at the HCBiFE (a), the Bi-PANI film electrode (b), and the BiFE(c) for 100 μg · $L^{-1}$ Cd(Ⅱ) and Pb(Ⅱ) in 0.1 mol/L acetate buffer (pH 4.7) (deposited at −1.1 V for 120 s)**

### 2.3 The optimal concentration ratio of aniline and Bi(Ⅲ) for preparation of the HCBiFE

Different HCBiFEs were fabricated by varying the concentration ratio of aniline and Bi(Ⅲ) in the plating solution. The concentration ratio was examined from 1 ∶ 1 to 1 ∶ 3, here the

concentration of aniline was fixed invariant at 0.005 mol/L with the concentration of Bi(Ⅲ) changing from 0.005 to 0.015 mol/L. The corresponding stripping peak currents of Pb(Ⅱ) and Cd(Ⅱ) at different HCBiFEs are displayed in Fig. 3. It is obvious that the highest stripping peak currents of both metals were achieved while the concentration ratio was 1 ∶ 2. Therefore, the concentration ratio of aniline and Bi(Ⅲ) in the plating solution was chosen as 1 ∶ 2 for the preparation of the hybrid composite bismuth film in order to achieve highest sensitivity.

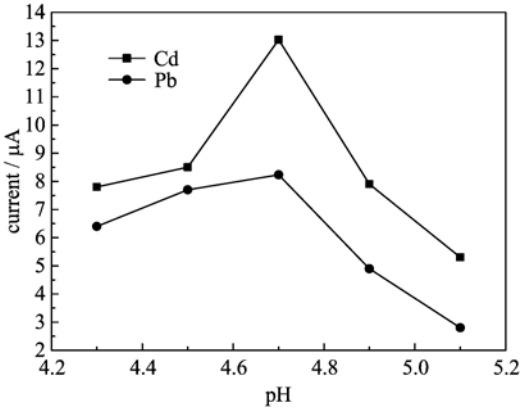



Other conditions are the same as those in Fig. 2

**Fig. 3　Effect of the concentration ratio of aniline and bismuth for preparation of HCBiFE on stripping currents of 50 μg · $L^{-1}$ Cd(Ⅱ) and Pb(Ⅱ)**

## 2.4　Effect of pH of electrolyte solution on stripping currents

The stripping peak currents of Pb and Cd were seriously influenced by the pH of the test solution. So the effect of pH on the stripping signals was investigated in the pH range 4.3 ～ 5.1. The dependence of the voltammetric peak currents of Pb and Cd on the pH of electrolyte solution is illustrated in Fig. 4. The stripping peak heights of Pb and Cd increased with the pH increasing from 4.3 to 4.7. But the stripping currents of both Pb and Cd decreased sharply when the pH exceeded 4.7 due to the pH-dependence of the conductivity of polyaniline. Therefore, pH 4.7 was chosen as the optimal acidity for the acetic buffer solution for stripping lead and cadmium.

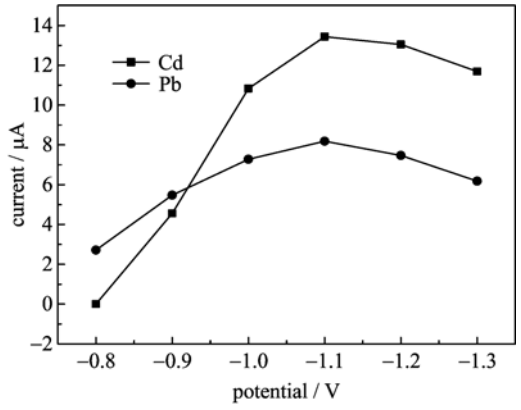



Other conditions are the same as those in Fig. 2

**Fig. 4　Effect of the pH of test solution on the stripping peak currents of 50 μg · $L^{-1}$ Cd and Pb at the HCBiFE**

## 2.5　The optimization of deposition potential and deposition time

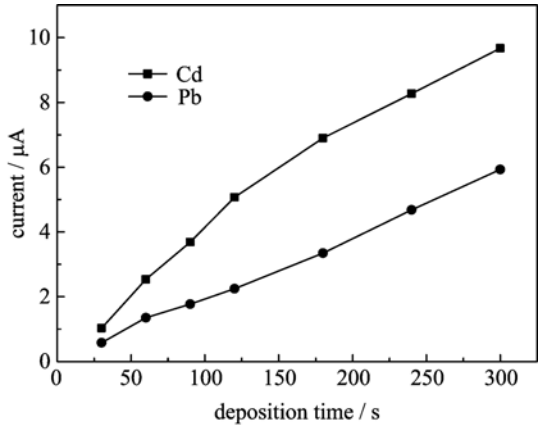
The effect of the deposition potential on stripping peak currents of Pb and Cd with the accumulation time of 120 s was studied, in 0.1 mol/L acetate buffer (pH 4.7) containing 50 μg · $L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ), in the potential range from −0.8 to −1.3 V. It can be seen from Fig. 5 that the peak currents of lead and cadmium increased gradually as the accumulation potential increased negatively from −0.8 to −1.1 V, and decreased slowly from −1.1 V to −1.3 V due to the hydrogen evolution on the HCBiFE. So the potential of −1.1 V was chosen as the optimal deposition potential for subsequent measurements.




Other conditions are the same as those in Fig. 2

**Fig. 5　Effect of deposition potential on stripping peak currents of 50 μg · $L^{-1}$ Cd and Pb at the HCBiFE**

As can be seen in Fig. 6, the stripping peak currents of 20 $\mu g \cdot L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ) increased almost linearly with the deposition time increasing from 30 to 300 s, which is in accordance with the theory of stripping analysis. And it is clear that the deposition saturation of both target metal ions on the composite bismuth film was not achieved actually[9]. Although a higher sensitivity could be obtained with further increase of deposition time, the analytical procedure would be prolonged. Form this point of view, 120 s deposition time was chosen as a compromise for the following measurements.




Other conditions are the same as those in Fig. 2

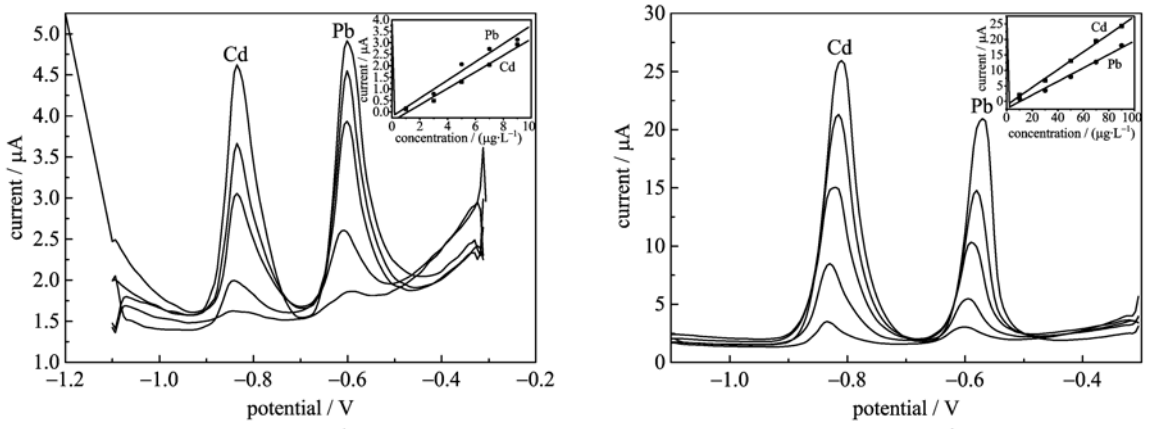
**Fig. 6 Effect of deposition time on stripping peak currents of 20 μg · $L^{-1}$ Cd and Pb at the HCBiFE**

## 2.6 Analytical performance of the HCBiFE

Under optimized conditions, the HCBiFE was examined by simultaneous determination of Pb(Ⅱ) and Cd(Ⅱ) with a series of standard solutions. Fig. 7(a) shows the stripping voltammograms of lead and cadmium in the concentration range from 1.0 to 9.0 $\mu g \cdot L^{-1}$, the resulting calibration curves for peak heights versus concentrations are inserted as an inset. The fitted linear equations were $y = -0.197 + 0.395x$ and $y = -0.408 + 0.358x$ ($x$/$\mu g \cdot L^{-1}$: concentration, $y$/$\mu$A: peak current), with the correlation coefficients of $R^2 = 0.985$ and 0.991 for Cd(Ⅱ) and Pb(Ⅱ) respectively. The deposition time was chosen to be 300 s due to the extreme low concentration. And Fig. 7(b) illustrates the stripping voltammograms of lead and cadmium in the concentration range from 10 to 90 $\mu g \cdot L^{-1}$, and the resulting calibration curves are also inserted as an inset. Similarly, the linear fitting equations obtained were $y = -1.178 + 0.285x$ and $y = -2.306\,5 + 0.2180\,5x$, with the correlation coefficients of $R^2 = 0.998$, and 0.993 for Cd(Ⅱ) and Pb(Ⅱ) respectively. Here the deposition time was chosen to be 120 s. The detection limits of Cd(Ⅱ) and Pb(Ⅱ) were 0.2 and 0.5 $\mu g \cdot L^{-1}$ respectively (S/N=3).

## 2.7 Reproducibility and stability of the HCBiFE

The reproducibility of the prepared hybrid composite bismuth film electrode was evaluated by 50 repetitive measurements of 50 $\mu g \cdot L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ), and the relative standard deviations (RSD) were 4.3% and 6.1% for Pb(Ⅱ) and




(a) concentration range 1~9 μg·$L^{-1}$ (deposition time 300 s)

(b) concentration range 10~90 μg·$L^{-1}$ (deposition time 120 s)

Other conditions are the same as those in Fig. 2

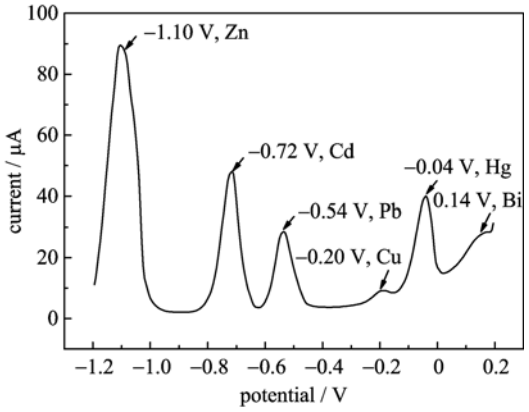
**Fig. 7 Stripping voltammograms for simultaneous determination of Cd and Pb obtained at the HCBiFE**

Cd(Ⅱ) respectively.

The stability of the prepared hybrid composite bismuth film electrode was examined by continuously working for 7 h, then being stored in deionized water. A month later, the stripping peak currents of 50 $\mu g \cdot L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ) in 0.1 mol/L acetic buffer solution were detected decreasing 3.2% and 4.9%, respectively. It is indicated that the prepared HCBiFE is quite stable in water and had good anti-mechanical denudation.

### 2.8 Interferences

The interferences of some metal ions on the stripping peak currents of 100 $\mu g \cdot L^{-1}$ Cd(Ⅱ) and Pb(Ⅱ) were examined. 5-fold of Zn(Ⅱ), Ni(Ⅱ), Co(Ⅱ), Cr(Ⅵ), Hg(Ⅱ) and equal concentration of copper were added into the test solution. The recorded stripping voltammogram is shown in Fig. 8. The peak potentials of all metals are labeled in the figure, but the stripping peaks of Ni(Ⅱ), Co(Ⅱ) and Cr(Ⅵ) do not appear because their reduced potentials are more negative than −1.2 V. It is clear that all added metal ions did not interfere with the analysis of cadmium and lead.




Solution: 0.1 mol/L acetic buffer solution containing 500 $\mu g \cdot L^{-1}$ Zn(Ⅱ), Ni(Ⅱ), Co(Ⅱ), Cr(Ⅵ), Hg(Ⅱ) and 100 $\mu g \cdot L^{-1}$ Cu(Ⅱ).
Deposition time: 120 s.
Other conditions are the same as those in Fig. 2

**Fig. 8 Stripping voltammogram of 100 $\mu g \cdot L^{-1}$ Pb(Ⅱ) and Cd(Ⅱ)**

In this work, the effects of some organic surfactants on stripping currents of 50 $\mu g \cdot L^{-1}$ Cd(Ⅱ) and Pb(Ⅱ) were also studied. The anionic surfactant sodium dodecyl sulfonate (SDS), cationic surfactant cetyltrimethyl ammonium bromide (CTAB) and nonionic surfactant Triton X-100 were chosen as representatives. The results are summarized in Tab. 1. Obviously, the stripping responses of both ions decreased less than 5% when the surfactant concentrations were less than 100 $\mu g \cdot L^{-1}$. But high concentration of surfactants would seriously interfere with the determination of Cd and Pb, especially for nonionic surfactants.

**Tab. 1 Influences of different types of surfactants on peak currents of Cd(Ⅱ) and Pb(Ⅱ)**

| Surfactants | concentration /($\mu g \cdot L^{-1}$) | peak current decrease/% | |
|---|---|---|---|
| | | Cd | Pb |
| SDS | 100 | 2.2 | 1.4 |
| | 1 000 | 8.5 | 7.4 |
| CTAB | 100 | 3.9 | 2.2 |
| | 1 000 | 11.2 | 12.5 |
| TritonX-100 | 100 | 5.0 | 4.2 |
| | 1 000 | 32.3 | 33.7 |

### 2.9 Application to real environmental water samples

A real environmental water sample was collected from Yanjinghu, a pool on USTC campus, filtrated with a 0.22 $\mu m$ membrane (purchased from Millipore) and adjusted to pH 4.7 before measurement. After that, the water sample was directly determined by standard addition method. Cadmium was not found in the sample, but lead was detected to be $(0.93 \pm 0.09)\ \mu g \cdot L^{-1}$. The results are summarized in Tab. 2.

**Tab. 2 The experimental result for detection of lead in water sample**

| sample | original /($\mu g \cdot L^{-1}$)[a] | added /($\mu g \cdot L^{-1}$) | found /($\mu g \cdot L^{-1}$)[b] | recovery /% |
|---|---|---|---|---|
| YANJINGHU | 0.93±0.09 | 2.0 | 2.82±0.10 | 94.5 |
| | | 4.0 | 5.23±0.08 | 107.5 |
| | | 8.0 | 9.44±0.11 | 106.4 |

【Note】 [a] Mean of three repetitive measurements for water sample
[b] Mean of three repetitive measurements at a 95% confidence level.

## 3 Conclusion

A novel and sensitive composite film electrode, organic-inorganic hybrid composite film electrode HCBiFE, is proposed for the stripping analysis of ultra-trace lead and cadmium by square wave anodic stripping voltammetry. The aniline could be polymerized intimately with crystalline bismuth due to the affinity between the crystalline bismuth and the structured polyaniline. It is revealed that the bismuth nanorods grow well in the grid meshes of the structured polyaniline. Therefore, the hybrid composite bismuth film could be tightly bonded onto the surface of GCE. The bismuth nanorods possess higher activity than the nanoparticles due to their high index crystal faces. The prepared HCBiFE in this work exhibits an excellent performance for the stripping analysis of lead and cadmium and shows a high sensitivity in acetic buffer solution. In summary, the HCBiFE is a promising alternative for MFE and common BiFE. Low cost, easy fabrication, lower toxicity, good linearity and reproducibility and environmental stability combine to make the prepared HCBiFE a possible practical use in on-site monitoring of heavy metals in environmental water.

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