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Disposable expanded graphite paper electrode with self-doped sulfonated polyaniline/antimony for stripping voltammetric determination of trace Cd and Pb

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Abstract

The conducting graphite electrode was fabricated by using the expanded graphite (EG) paper with screen-printing technique, onto which self-doped sulfonated polyaniline (SPAN) was electropolymerized via aniline and *m*-aminobenzenesulfonic acid monomers, and the Sb/ SPAN/EG electrode was obtained by electrodepositing Sb onto the copolymer modified EG electrode. The sensitivity of disposable EG electrode was improved by using two-step ex-situ fabricating procedure, in which the anodic doping of $SbCl_4^-$ for the SPAN film was kept at +0.3 V for 300 s and then reduced at -0.5 V for 100 s in solution containing 10 mg L^{-1} Sb(Ⅲ) and 0.5 M hydrochloric acid. The disposable Sb/SPAN/EG electrodes were used for the simultaneous determination of trace lead and cadmium by differential pulse anodic stripping voltammetry. The stripping currents increased linearly when the metal concentration was in a range of 2～70 μg L^{-1}, and the limits of detection were 0.20 μg L^{-1} for Pb(II) and 0.41 μg L^{-1} for Cd(II) at the preconcentration time of 180 s, respectively. The proposed disposable working electrode, as new style of “mercury-free” electrode for heavy metal measurement, exhibits encouraging properties for the practical use, such as the low cost, good reproducibility.

Keywords: Antimony modified electrode, Self-doped sulfonated polyaniline, Differential pulse anodic stripping voltammetry, Heavy metals

1. Introduction

Lead and cadmium in the environment and food pose a great threat to living organisms due to their non-biodegradability and persistence. So the method for the determination of heavy metals is of great significance.[1] Over the past few decades, the analytical methods for the determination of trace amounts of toxic heavy metals were developed, such as atomic absorption spectrometry (AAS),[2,3] atomic fluorescence spectrometry,[4] inductively coupled plasma optical emission spectrometry (ICP-OES) and so on.[5] However, all these methods have some drawbacks such as time-consuming, high cost, demand for complex instrumentation and unsuitability for on-field analysis.[6] Electrochemical methods, particularly anodic stripping voltammetry (ASV), have been proven to be a powerful tool for fast determination of metal ions in complex samples due to their high sensitivity, easy operation, and low cost of analysis.[7] Differential pulse anodic stripping voltammetry (DPASV) is widely used to detect trace heavy metals, which is based on a preconcentration by electrodeposition of metallic ions from a sample solution onto a working electrode surface, followed by anodic stripping of the electrode surface into the sample solution. Replacement of conventional electrochemical cells by screen-printed carbon electrodes connected to miniaturized potentiostats is a main trend in the shift of lab electrochemical equipments to hand-held field analyzers.[8] The screen-printed carbon electrodes produced by printing different inks on plastic or ceramic supports are gaining widespread applicability for electrochemical analysis, especially for the determination of heavy metals. Mercury electrodes have been traditionally employed for achieving high reproducibility and sensitivity of the anodic stripping voltammetry.[9] As Hg is toxic, its incorporation into sensors poses problems, particularly from the viewpoint of disposable electrode. Consequently, other mercury-free SPCEs have been developed by employing alternative metals films (e.g. gold, bismuth) which are less toxic.[10,11] Antimony film electrodes have been an attractive new subject of electroanalytical performance, such as favorably negative overpotential of hydrogen evolution, convenient operation in relatively strong acidic medium ($pH<2$) and interestingly low stripping signal for antimony itself.[12] the antimony based electrodes fabricated by using different modifications and preparation routes have been used in both adsorptive stripping mode[13-15] and constant current stripping chronopotentiometry.[16]

Recently, modified electrodes based on incorporation of conducting polymer films have received considerable attention for detection of trace heavy metals due to their superior electrical conductivity, good adhesion property and suitable structural characteristics.[17-20] The conducting polyaniline (PAN) can be electrochemically coated on the surfaces of glassy carbon electrode and form a porous substrates of Bi, Hg, Au for the detection of trace heavy metals.[21-26] The property of conducting PAN polymer could be improved by introducing new functional groups into the polymer.[27] The copolymerisation appears as an interesting tool to PAN modification because monomers less reactive than aniline (or unreactive) can be introduced in the polymer chain. Furthermore, the degree of modification can be controlled varying the feed composition in the synthesis, and the properties of the new materials can be tailored. The electrochemical copolymerization of aniline and aniline derivates, such as aniline with metanilic, orthanilic, and *m*-aminobenzoic acids could form a stable polymer film onto the conducting substrates, showing the redox activity up to pH 10.[28]

Expanded graphite (EG), which prepared from natural graphite by chemical treatment, kept most excellent characteristics of natural graphite and overcame hard, fragile and some other defects of natural graphite. The EG electrodes was successfully applied to electrochemical sensors and electrical double-layer capacitors.[29-31] In this work, the disposable conducting graphite electrode was fabricated by using the expanded graphite paper with screen-printing technique, onto which the copolymer of aniline and *m*-aminobenzenesulfonic acid was electrochemically deposited, and followed by modification of antimony. The electrochemical characteristics of expanded graphite electrode with self-doped sulfonated polyaniline/ antimony were investigated in detail, and successfully applied to measure trace heavy metals by using differential pulse anodic stripping voltammetry.

2. Experimental

2.1. Reagents

Aniline was purchased from Tianjin Bodi Chemical Co., LTD, and was distilled before use. Stock solutions of antimony(III) trichloride, lead(II) nitrate, and cadmium(II) nitrate, all having a concentration of 1.0 g L^{-1}, were prepared and stored at room temperature. Sodium acetate and acetic acid were purchased from Taishan Chemical Factory Co., LTD. 0.1 M acetate buffer (pH 4.5) were used as supporting electrolyte. *m*-Aminobenzenesulfonic acid (metanilic acid) and other chemicals used were of analytical reagent grade. All aqueous solutions were prepared in Milli-Q ultrapure water (18.25 MΩ cm).

2.2. Apparatus

Electrochemical measurement experiments were performed with a CHI660D electrochemical workstation

(Chenhua Instrumental Corporation, Shanghai) by using a three-electrode electrolytic cell. The Sb/SPAN modified graphite paper electrode (3 mm in diameter) used as the working electrode. A KCl saturated calomel electrode and a platinum plate were used as the reference electrode and the counter electrode, respectively. All electrochemical measurements were carried out in a 25 mL cell at room temperature. The electrochemical impedance spectroscopy (ESI) of polymer modified graphite paper electrode was measured by using the superimposed sinusoidal voltage signal of 5 mV amplitude, and data were collected within the frequency range of 10^5 to 10^{-2} Hz, taking five points per decade.

2.3. Sample preparation

The water samples were collected from tap water in our laboratory and Xiangjiang river. For the determination of Pb(Ⅱ) and Cd(Ⅱ), all water samples were filtered with a 0.45 μm membrane (Millipore) in advance, and then 20 mL of the water sample and 5 mL acetate buffer solution were placed in the cell and the analysis was carried out as described below. ICP-MS experiments were performed with ELAN6100 (PerkinElmer Sciex) using internal standards.

2.4. Procedure

2.4.1. Preparation of EG paper electrode with screen-printing method

Commercially available EG paper (thickness of 0.1 mm, SiChuan Chemshine Carbon Co.,Ltd) was socked in 1:1 HNO_3 solution for 15 min, and then rinsed with distilled water. One face of EG paper was covered with PVC plate (thickness of 0.5 mm), and cut into rectangle electrodes (10 mm × 5 mm), a protective insulator polymer (704 silicone rubber) was coated onto the another face of EG electrode using screen-printing method, and the test electrode with diameter of 3 mm was obtained (Fig. 1).

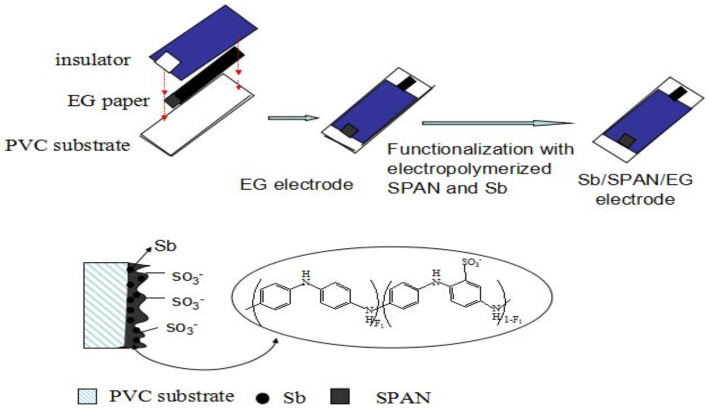

Fig. 1. Illustration of Sb/SPAN/EG electrode preparation and modification.

2.4.2. Modification of EG paper electrode

For modification, the EG paper electrode was used as a working electrode in an aqueous solution containing 0.04 M aniline, 0.01 M *m*-aminobenzenesulfonic acid and 0.5 M sulfuric acid. The electrochemical copolymerization of aniline and *m*-aminobenzenesulfonic acid was done at the EG surface by continuous potential cycling for 10 min within potential limits of -0.2 ~ 1.0 V, and self-doped sulfonated polyaniline (SPAN) film was coated onto the surface of EG electrode.

Three types of Sb/SPAN/EG electrodes were prepared: (1) SPAN/EG electrode was immersed in a 25 mL cell containing 10 mg L^{-1} Sb(Ⅲ) and 0.5 M hydrochloric acid, keeping the potential at -0.5 V for 100 s for the deposition of antimony (namely as one-step ex-situ prepared Sb/SPAN/EG electrode). (2)Before the antimony electrodeposition, the polymer film was kept at +0.3 V for 300 s in a solution containing 10 mg L^{-1} Sb(Ⅲ) and 0.5 M hydrochloric acid for the anodic doping of $SbCl_4^-$, and then the potential of SPAN/EG electrode was biased at -0.5 V for 100 s for the electrodeposition of antimony (namely as two-step ex-situ prepared Sb/SPAN/EG electrode). (3) In DPASV measurement, the Sb/ SPAN/EG electrode was prepared in situ on a SPAN/EG electrode in acetate buffer solution (pH 4.5) containing appropriate amounts of Pb(Ⅱ), Cd(Ⅱ) and Sb(III) ions (namely as in-situ prepared Sb/SPAN/EG electrode).

2.4.3. Determination of Pb(Ⅱ) and Cd(Ⅱ)

The cleaned Sb/SPAN/EG electrodes, the reference and counter electrode were immersed into a 25 mL electrochemical cell, containing appropriate amounts of Pb(Ⅱ), Cd(Ⅱ) and 5 mL of 0.1 M acetate buffer solution (pH 4.5). The deposition potential (-1.1 V) was applied to the working electrode for 180 s, while the solution was stirred. Following the preconcentration period, the stirring was stopped. After 20 s quiet time, the voltammogram was recorded at a positive-going differential pulse scan between -1.0 ~ -0.3 V with amplitude of 50 mV, pulse width of 50 ms and potential increment of 5 mV. For the investigation of pH effect, the pH value of test solution was adjusted by adding 0.1 M Sodium acetate or 0.1 M acetic acid solution, and measured with pH meter. All experiments were performed at room temperature.

3. Results and Discussion

3.1. Electrochemical responses of EG, SPAN/EG and Sb/SPAN/EG electrode

The screen-printed carbon electrodes are disposable devices produced through the screen-printing technology, which consists of a layer-by-layer deposition of different inks upon a solid substrate. For the improvement of carbon electrode conductivity, the silver ink is usually printed as conductive track, resulting in the increase of disposable electrode cost. In this study, the flexible EG paper was used to fabricate the low-cost working electrode, and electrochemically modified with polyaniline and antimony. Self-doped PAN derivatives present an important class of conducting polymers, bearing ionizable negatively charged functional groups, most frequently sulfonateones.[27,28] These negatively charged groups act as intramolecular dopant anions that are able to compensate positive charges at protonated nitrogen atoms of the polymer backbone, thus replacing auxiliary solution dopant anions. This inner anion doping determines many distinctive properties of self-doped PAN derivatives. In contrast to PAN, which shows its redox activity at solution pH not exceeding 3 or 4, self-doped derivatives are active in a broad range of solution pH, extended to higher values, in some cases up to pH 14. Fig. 2 shows the cyclic voltammograms for the bare EG electrode, SPAN/EG electrode, and Sb/SPAN/EG electrode (first scans) in 0.1 M acetate buffer solution (pH 4.5). In comparison with the bare EG electrode, both the SPAN/EG and Sb/SPAN/EG electrode produced the relatively high background currents. The charge of the double layer and faradaic processes are the contributing factors to the background current. Since no significant redox peaks were observed in cyclic voltammograms for the potential ranging from -1.3V to -0.3 V, the charge of the double layer, which is proportional to the surface area, was the main contributing factor. In Fig. 2, the background current for both the bare EG and SPAN/EG electrode increased rapidly at the potential below -1.2 V, while Sb/SPAN/EG electrode exhibited the lower background current and more negative hydrogen evolution potential than the SPAN/EG electrode.

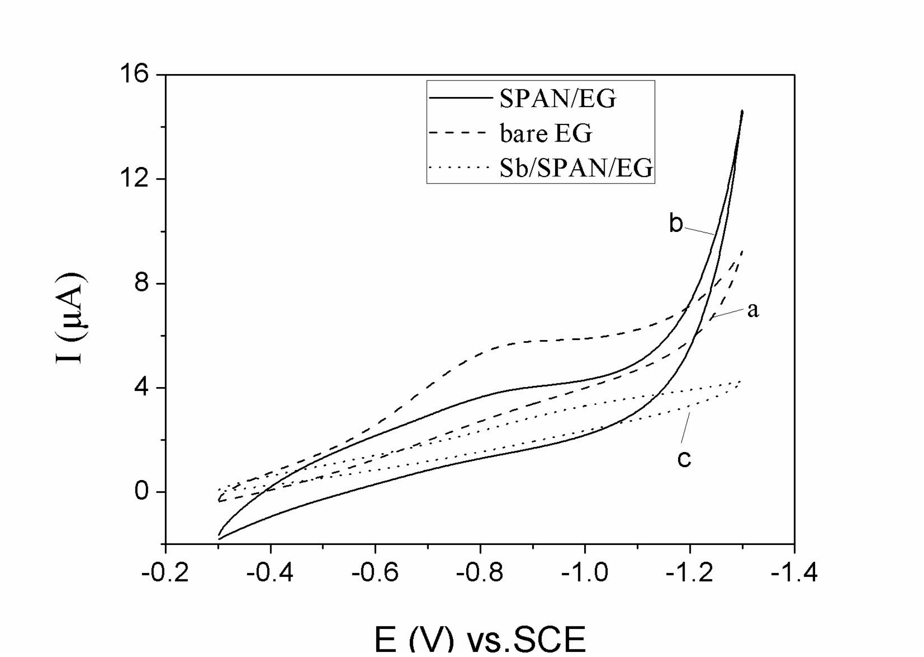

Fig. 2. Cyclic voltammograms for the different working electrodes with a scan rate of 50 mV s^{-1} in 0.1 M acetate buffer solution (pH 4.5). (a) bare EG electrode, (b) SPAN/EG electrode, and (c) Sb/SPAN/EG electrode.

At the film-solution interfaces the charge transfer resistance of the Sb/SPAN coatings is affected by the thickness, specific surface area, conductivity, doping level of SPAN. In Nyquist plots (Fig.3), the diameter of the semicircle represents the transfer resistance of charge between the SPAN coating and electrolyte. It can be seen that the transfer resistance for Sb/SPAN coating decreased compared to the SPAN coating.

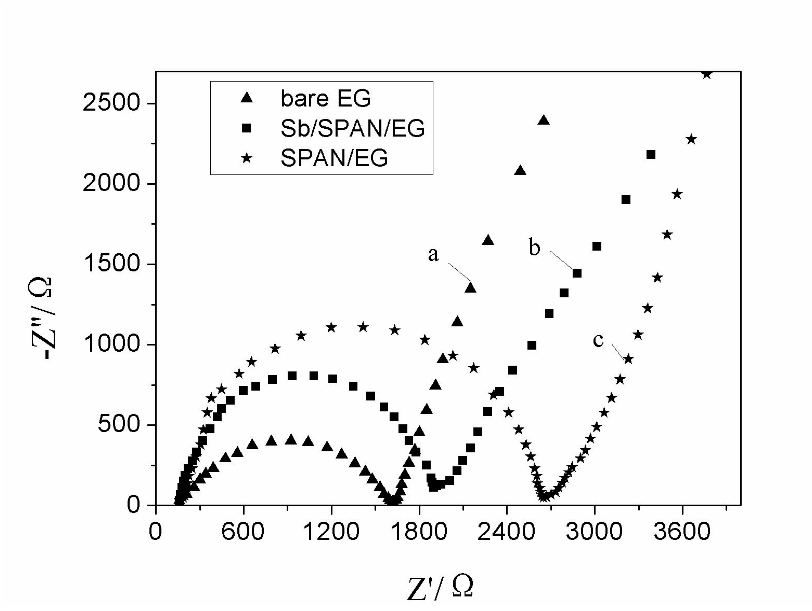

Fig. 3. The EIS of (a) bare EG electrode, (b) Sb/SPAN/EG electrode, and (c) SPAN/EG electrode in 0.1 M acetate buffer solution (pH 4.5) containing 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ).

3.2. Anodic stripping responses of different working electrodes to Pb(Ⅱ) and Cd(Ⅱ) ions

Fig. 4 shows the differential pulse voltammetric responses of 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ) at the bare EG electrode (a), SPAN/EG electrode (b), and Sb/SPAN/EG electrode (c). The sharp and separated peaks were observed for the anodic stripping curves of Pb(Ⅱ) and Cd(Ⅱ) at above test electrodes, and the stripping peak currents for Pb(Ⅱ) and Cd(Ⅱ) at the SPAN/EG electrode (curve b) are larger than that obtained at the bare EG electrode, which can be attributed to the fact that PAN films modified on the EG have unique three-dimensional structures with a large number of microgaps and micropores. These porous structures can offer a large specific surface area, so the PAN films can be served as an excellent supporting material for chemical sensors.[17] Additionally, it was found that the existence of the -SO_3^- groups bonding to the phenyl rings in copolymer produced the electrochemical oxidation of aniline and *m*-aminobenzenesulfonic acid monomers, and the anionic species pendant on SPAN could be used to anchorage cationic or protonated species in SPAN modified-electrodes, increasing their detection sensitivity or selectivity of the electrodes. In comparison with the bare EG and SPAN/EG electrode, the stripping signals of both metal ions on the Sb/SPAN/EG electrode have been significantly enhanced (curve c). It may be due to the fact that antimony exhibits the strong adsorptive ability to the target metal ions and favorably negative overpotential of hydrogen evolution.

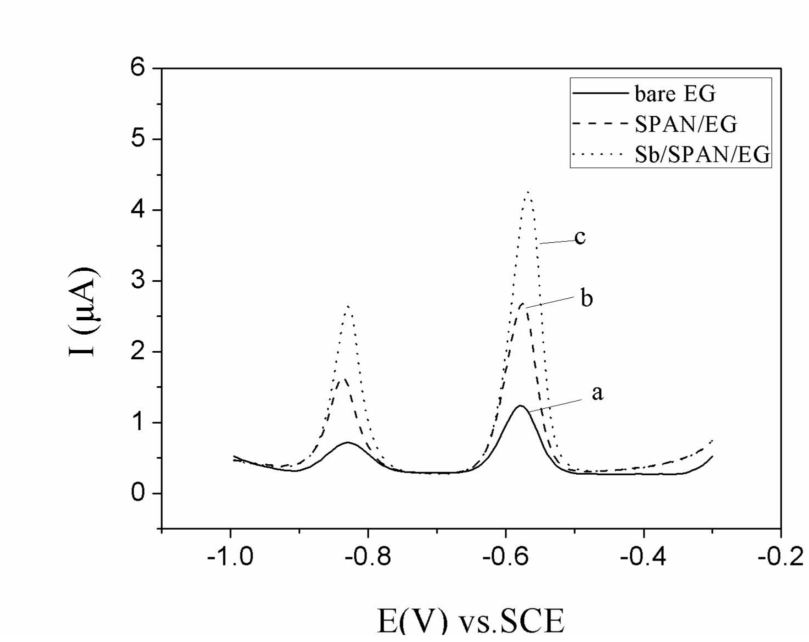

Fig. 4. DPASV signals for the detection of 20 μg L^{-1} Pb (II) and Cd (II) in 25 mL electrochemical cell containing 5 mL 0.1 M acetate buffer solution (pH 4.5) form: (a) bare EG electrode, (b) SPAN/EG electrode, (c) Sb/SPAN/EG electrode. Deposition potential: -1.1 V; deposition time: 180 s; amplitude: 50 mV; pulse width: 50 ms; potential increment: 5 mV.

Three procedures were used for the preparation of Sb modified SPAN/EG electrode, and the stripping responses of the in-situ prepared Sb/SPAN/EG electrode, one-step ex-situ prepared Sb/ SPAN/EG electrode, two-step ex-situ prepared Sb/SPAN/EG electrode were investigated (Table 1). As for the porous SPAN composite modified electrodes, the reduced heavy metals can be deposited and trapped at both the conducting substrate and the internal active sites of coating near surface during the preconcentration. However, the oxidized ions from the trapped heavy metal deposits at the internal layer of coating cannot easily or completely diffuse out of the modified electrode surface during the stripping, and the residual metals can influences the results from the subsequent measurements. As can be seen in Table 1, the ex-situ prepared Sb/SPAN/EG electrodes gave an improved reproducibility of the anodic stripping signals compared with the in-situ prepared Sb/SPAN/EG and SPAN/EG electrode. Especially, the two-step ex-situ prepared Sb/SPAN/EG electrode produced the highest value of the stripping peak current and the lowest value of relative standard deviation (RSD). A possible explanation is that Sb particles are deposited on both the SPAN coating and the bare EG surface exposed through the porosities in the SPAN coating during the anodic doping of $SbCl_4^-$ for the preparation of Sb/SPAN/EG electrode, producing the more Sb sites for the heavy metal ions electrodeposition. As can be seen in Fig. 5, the transfer resistance for two-step ex-situ

Sb/SPAN/EG electrode decreased compared to the one-step ex-situ Sb/SPAN/EG and SPAN/EG electrode.

Table 1

Stripping responses of different Sb modified SPAN/EG electrodes to Pb(II) an Cd(II) ions

	two-step ex-situ prepared Sb/ PAN/EG		one-step ex-situ prepared Sb/ PAN/EG		in situ prepared Sb/ PAN/EG		PAN/EG		Sb/EG electrode	
	Stripping current (μA)	RSD (%)	Stripping current (μA)	RSD (%)	Stripping current (μA)	RSD (%)	Stripping current (μA)	RSD (%)	Stripping current (μA)	RSD (%)
Pb(Ⅱ) 20 μg L^{-1}	3.5±0.32	4.3	3.1±0.68	9.5	2.7±0.68	11	2.3±0.65	11	2.04±0.71	12.5
Cd(Ⅱ) 20 μg L^{-1}	2.4±0.22	3.4	2.0±0.52	8.6	1.3±0.32	9.6	1.03±0.33	12	1.01±0.35	12

All data obtained in five tests

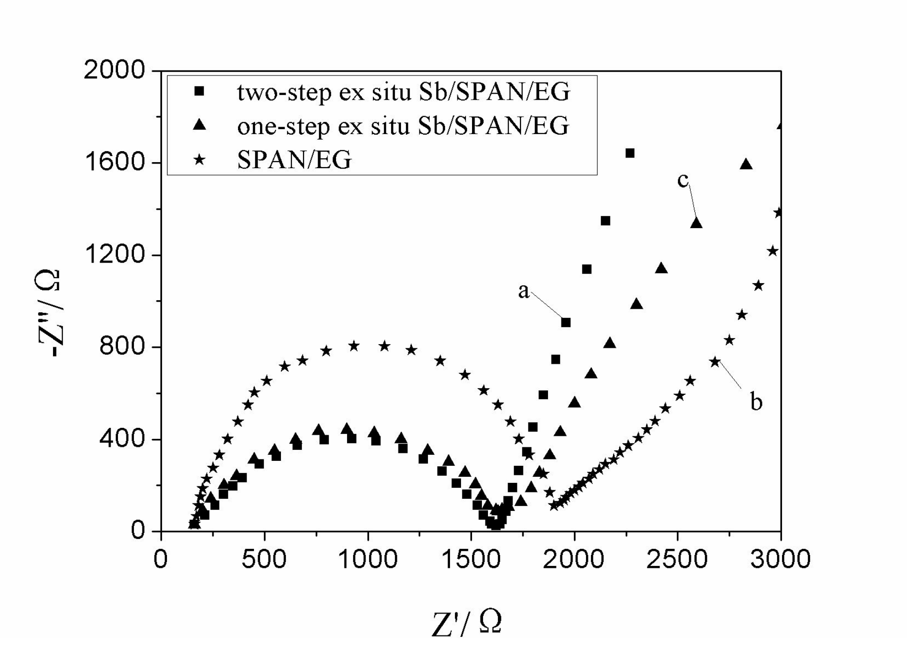

Fig. 5. The EIS of the (a) two-step ex situ Sb/SPAN/EG electrode , (b) SPAN/EG electrode and (c) one-step ex situ Sb/SPAN/EG electrode in 0.1 M acetate buffer solution (pH 4.5) 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ).

3.3. Effects of experimental variables

3.3.1. SPAN film thickness

In the present work, the sulfonated polyaniline (SPAN) films were prepared by a simple electropolymerization process from a feed solution containing both aniline and metanilic acid as comonomers, and a stable and adhesive copolymer film was coated on the surface of EG paper electrode by using 4:1 of the ratio for aniline to *m*-aminobenzenesulfonic acid monomer. It has been reported that the composition of electrodeposited SPAN films, i.e. the ratio of sulfonated and unsulfonated aniline units in the copolymer chain, depend greatly on many variables like the ratio of both comonomers in the feed solution, and the solubility decreases with increasing the aniline molar fraction in the copolymer.[28] The thickness of SPAN film can be controlled by changing the monomer concentration or the electrodeposition time. Electropolymerization of SPAN was performed by continuous potential cycling for 10 min within potential limits of -0.2 to 1.0 V at potential sweep rate of 50 mV s^{-1}. The effect of SPAN films thickness on the response of modified electrode was displayed in Fig. 6, which shows the stripping peak currents to 20 μg L^{-1} Pb(II) and Cd(II). When the position time was less than 600 s, the stripping signals of two target metal ions increased with the deposition time increasing. However, when the SPAN layer was beyond a certain thickness, the stripping currents of two target metal ions decreased with the increase of SPAN deposition time. This is in agreement with that reported that the stripping responses would first increased and then weaken as the aniline concentration was increased.[17]

3.3.2. Sb(III) ion concentration

The amount of deposited antimony on the polymer modified EG electrode relied on the Sb(III) concentration in the solution and electrodeposition time. The effect of antimony concentration on the responding currents for the determination of Pb(II) and Cd(II) is depicted in Fig.7, where the stripping signals for Cd(II) increased with the increasing concentration of Sb(III) in the solution, up to 6 mg L^{-1} of Sb(III) and then started to decrease, whereas the current for Pb(II) increased up to 10 mg L^{-1}. Thus, the concentration of 10 mg L^{-1} Sb(III) is selected.

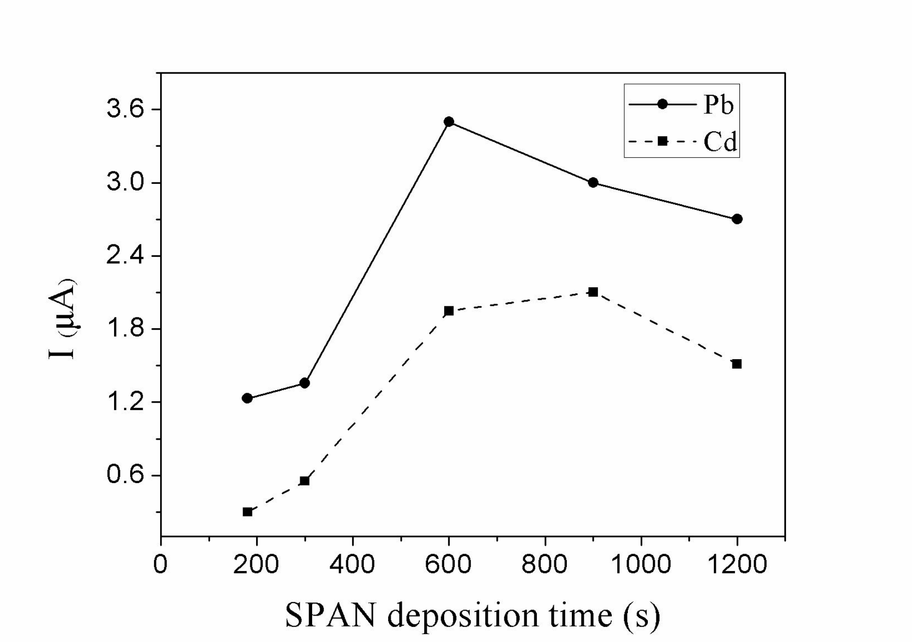

Fig. 6. Effect of SPAN deposition time on stripping peak currents of 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ).

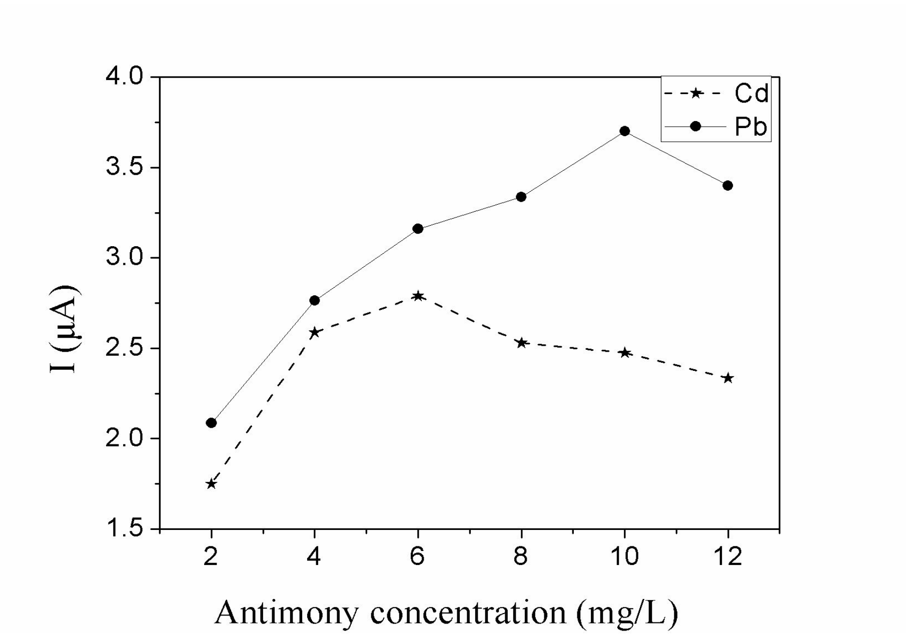

Fig. 7. Effect of antimony concentration on stripping peak currents of 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ).

3.3.3 Preconcentration potential

As shown in Fig. 8, the stripping responses of Pb(II) and Cd(II) were found to occur in the range of -1.4 and -0.9 V. As the preconcentration potential decreased from -0.9 to -1.1 V, the stripping peak currents increased due to more reductions of the two target metal ions. But the currents of Pb(II) and Cd(II) increased slowly even decreased when the preconcentration potential became more negative than -1.1 V. The evolution of hydrogen gas started at -1.2 V and could reduce the surface activity of the Sb/SPAN/EG electrode. Therefore, a preconcentration potential of -1.1 V was chosen as optimum for determination of Pb(II) and Cd(II).

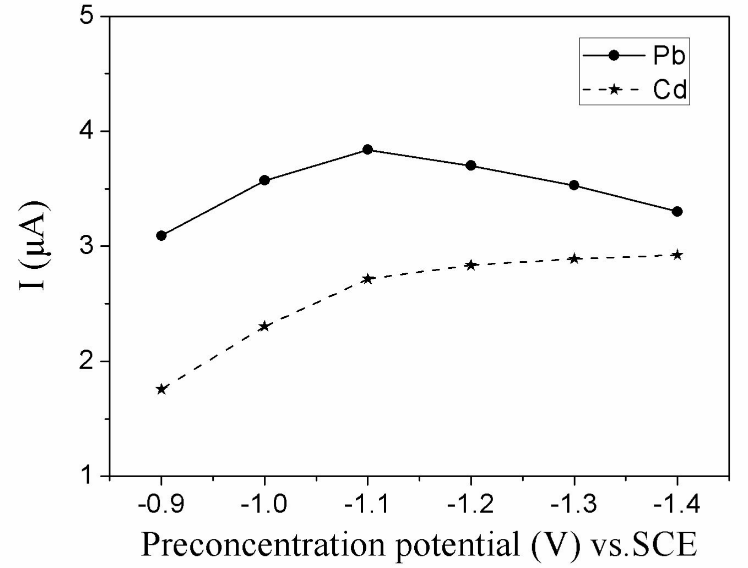

Fig. 8. Effect of preconcentration potential on stripping peak currents of 20 μg L^{-1} Pb(II) and Cd(II).

3.3.4 Preconcentration time

The influence of deposition time on the tripping peak signals of Pb(II) and Cd(II) were studied from 60 s to 420 s. The responses of both metal ions increased quickly with the increase of the deposition time up to 300 s. When the deposition time was more than 300 s, the curve slop slightly decreased. Taking into both of the sensitivity and the efficiency, the deposition time of 180 s was used in the further experiments.

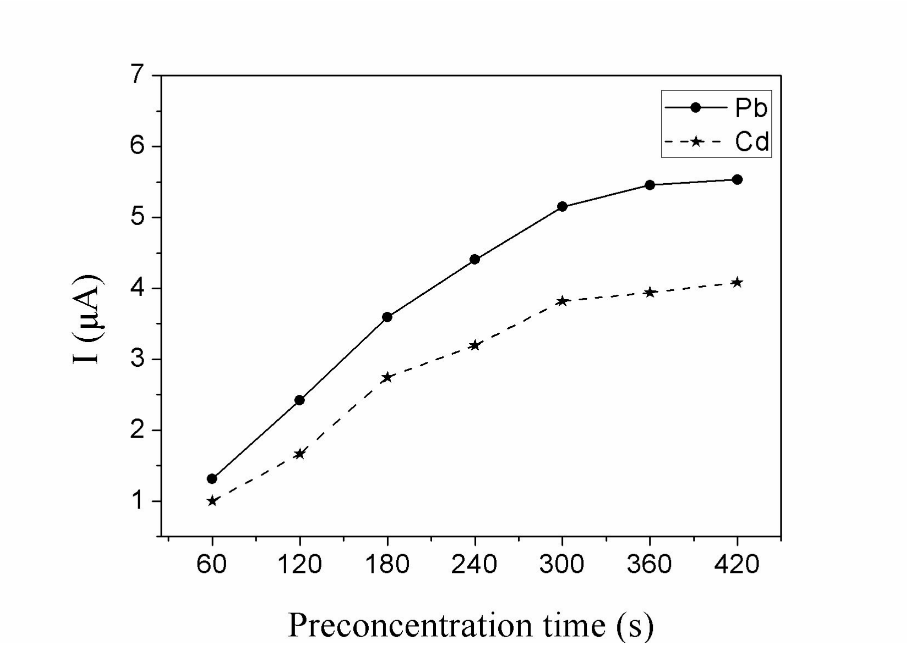

Fig. 9. Effect of preconcentration time on stripping peak currents of 20 μg L^{-1} Pb(II) and Cd(II).

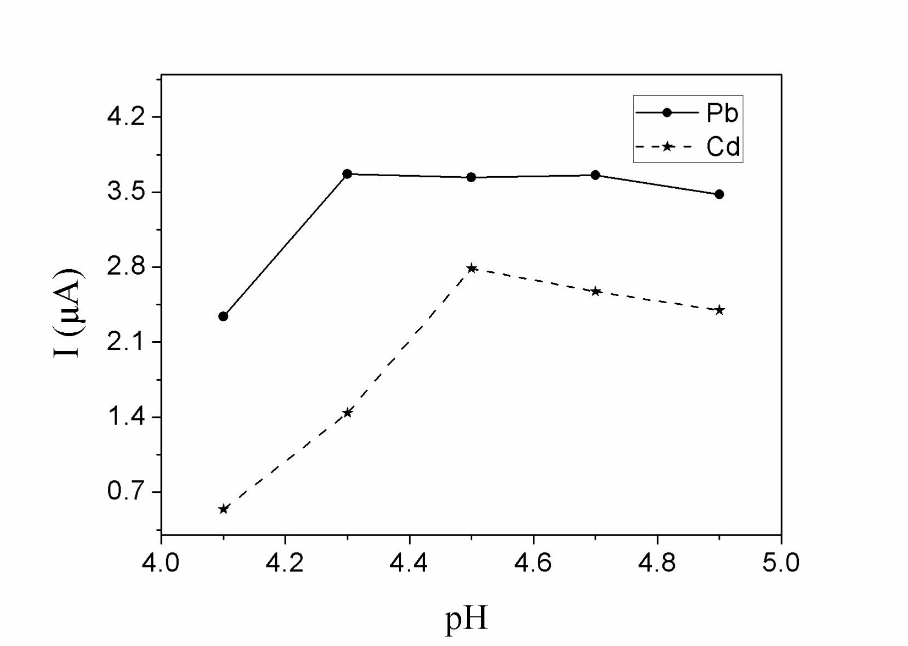

Fig. 10. Effect of pH on stripping peak currents of 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ).

3.3.5 pH

The influence of pH on the stripping peak current of Pb(Ⅱ) and Cd(Ⅱ) was illustrated in Fig. 10. The peak currents increase with the increase of solution pH up to 4.5, and then drops. So the best signals appeared at pH 4.5, which was a more mildly acidic condition. This result is similar to the reported pH values of other electrodes for the measurement of Pb(Ⅱ) and Cd(Ⅱ).[6] The following experiments were carried out in a pH 4.5 acetate buffer solution.

3.4. Simultaneous determination of Pb(Ⅱ) and Cd(Ⅱ)

The calibration curves for the simultaneous determination of Pb(Ⅱ) and Cd(Ⅱ) on the Sb/SPAN/EG electrode were studied under the optimized conditions. A series of stripping peak currents for different concentrations of two metal ions were shown in Fig. 11. It can be seen that the stripping currents and the concentration of Pb(Ⅱ) and Cd(Ⅱ) exhibited a great linear relation over the range from 1 to 70.0 μg L^{-1}. The calibration curves and correlation coefficients are $I = 0.1474\ C - 0.0078$, $r = 0.9981$ for Pb(Ⅱ), and $I = 0.1324\ C - 0.2412$ (C: μg/L , I: μA), $r = 0.9997$ for Cd(Ⅱ) , respectively. Repetitive measurements of 20 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ) are showed good reproducibility with the relative standard deviations less than 3.01% and 5.33%, respectively (n = 10). The detection limits of Pb(Ⅱ) and Cd(Ⅱ) are 0.20 μg L^{-1} and 0.41 μg L^{-1} (S/N=3), respectively. To test the long-time stability of the working electrode, fifty electrodes were prepared and stored in black plastic box at the room temperature. The tests for 20 μg L^{-1} Pb(Ⅱ) solution were done in different days within 100 days. The RSD obtained was not more 5% (five electrodes for each test), which means no obvious effect of the storage on the response of present modified electrode in single use.

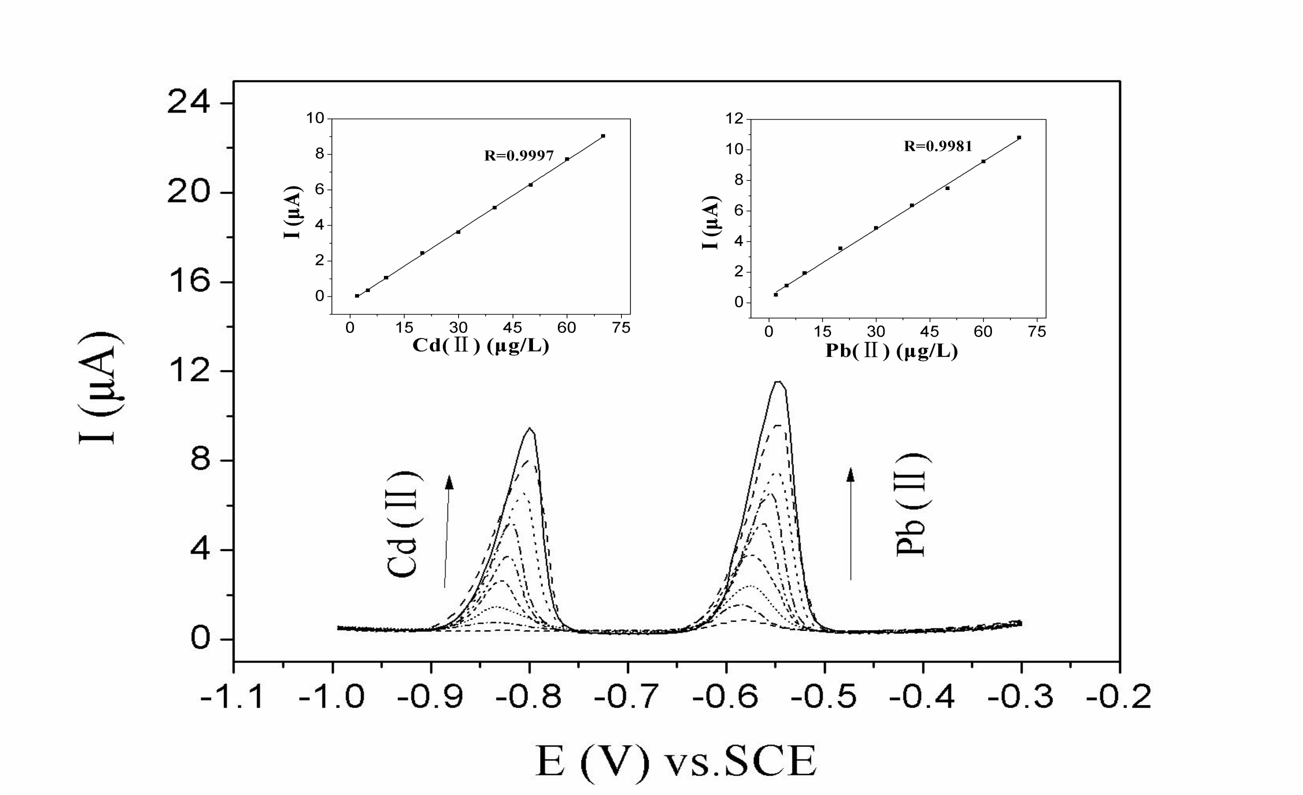

Fig. 11. DPASVs for additions of 2, 5, 10, 20, 30, 40, 50, 60 and 70 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ) in 0.1 M acetate buffer solution (pH 4.5). The insets shows the corresponding calibration curves for determination of Pb(Ⅱ) and Cd(Ⅱ), respectively.

3.5. Interference study

The interference ions were studied under the optimal conditions with 30 μg L^{-1} Pb(Ⅱ) and Cd(Ⅱ). The ratios of interference to Pb(Ⅱ) and Cd(Ⅱ) for a ± 5.0% peak currents change are listed as follows: 1000 fold for K(Ⅰ), Na(Ⅰ), Ca(Ⅱ), Cl^-, SO_4^{2-}; 200 fold for Mg(Ⅱ),Fe(III), Mn(Ⅱ), Al(III), NO_3^-, CO_3^{2-}; 100 fold for Zn(Ⅱ), As(III), Cr(Ⅵ), F^-; 50 fold for Hg(Ⅱ), Cu(Ⅱ).

3.6. Application

The Sb/SPAN/EG electrode was used for the determination of Pb(Ⅱ) and Cd(Ⅱ) in water samples (Table 2). 5 mL 0.1 M acetate buffer solution (pH 4.5) and 20mL water were added to 25 mL electrochemical cell for the determination of metal ions. The concentrations of Pb(Ⅱ) in river water and tap water were 2.62 μg L^{-1} and 2.13 μg L^{-1}, respectively, which were in good agreement with the values of 2.63 μg L^{-1} and 2.14 μg L^{-1} obtained by measurement of ICP-MS. While the concentration of Cd(Ⅱ) was not determined.

Table 2 Determination results in water samples

Sample	Original	Original	Added	Added	Pb(Ⅱ)			Cd(Ⅱ)		
	Pb(Ⅱ) (μg L^{-1})	Cd(Ⅱ) (μg L^{-1})	Pb(Ⅱ) (μg L^{-1})	Cd(Ⅱ) (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	RSD (%)	Found (μg L^{-1})	Recovery (%)	RSD (%)
River water	2.62	N.D.	5.00	5.00	7.57	99.0	2.71	4.85	97.0	3.43
Tap water	2.13	N.D.	5.00	5.00	7.20	101.4	2.63	4.91	98.2	2.54

N.D.: not detected.

4. Conclusions

In this work, the working electrode was fabricated by using the expanded graphite paper with screen-printing technique, and modified with sulfonated polyaniline and metallic Sb. The sensitivity of the Sb/SPAN/EG electrode was improved by using two-step ex-situ fabricating procedure, in which the anodic doping of $SbCl_4^-$ for the SPAN film was done before the electrochemical reduction of $SbCl_4^-$. The simultaneous detection of lead and cadmuim was successfully done by DPASV method based on the Sb/SPAN/EG electrode. The developed disposable Sb/SPAN/EG electrode possesses some advantages such as low cost, good reproducibility, and can be expected to find applications in electroanalytical assays.

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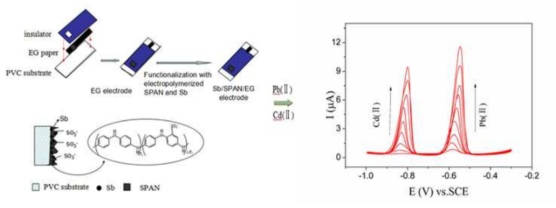

Disposable expanded graphite paper electrode with self-doped sulfonated polyaniline/antimony for stripping voltammetric determination of trace Pb and Cd.