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Selenium-coated carbon electrode for anodic stripping voltammetric determination of copper(II)

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Abstract In this work, we describe a new and promising type of selenium film electrode for anodic stripping voltammetry. This method is based on formation of copper selenide onto an *in-situ* formed selenium-film carbon electrode, this followed by Osteryoung square-wave anodic stripping voltammetry. Copper(II) is also *in-situ* electroplated in a test solution containing 0.01 mol L^{-1} hydrochloric acid, 0.05 mol L^{-1} potassium chloride and 500 µg L^{-1} Se(IV) at a deposition potential of −300 mV. Well-defined anodic peak current observed at about 200 mV is directly proportional to the Cu(II) concentration over the range of 1.0–100 µg L^{-1} under the optimized conditions. The detection limit (3 sigma level) is 0.2 µg L^{-1} Cu(II) at 180 s deposition time. Relatively less interferences are shown from most of metal ions except for antimony(III). The proposed method can be applied to sample analyses of river water and oyster tissue with good accuracy.

Keywords Selenium-film electrode; stripping analysis; copper determination

Introduction

Stripping voltammetry has been accepted to be one of the most sensitive and convenient electrochemical techniques for the determination of heavy metals in aqueous medium at trace concentration levels [1]. Conventionally, hanging mercury drop electrodes and mercury film electrodes [2] have been used as the working electrodes for stripping voltammetric analysis of metals. Due to high toxicity of mercury, much effort has recently been directed into developments of the so-called “mercury-free” electrodes, which include bismuth [3-6], antimony [7,8], lead [9] and tin [10] that have relatively wide potential windows at the negative region depending on the standard redox potentials. Among several kinds of electrode materials developed, the Bi- and Sb-film electrode have been getting more and more recognized as useful and feasible alternatives to the toxic mercury-based electrodes in the direct determination of metals such as Cd [3], Pb [3], Zn [3], In [11], Tl [11], Co [12], Ni [13], As [14] and Se [15] by anodic or cathodic stripping analysis. Several review articles describe the characteristics of the mercury-free electrodes, and their electroanalytical performances and a variety of applications [16-19]. However there is one drawback that the Bi- and Sb-film electrodes have relatively negative anodic limits (around −0.20 V *vs.* Ag/AgCl) restricted by dissolution of the metal electrodes. For example, a considerably large anodic peak due to bismuth dissolution appeared just before the Cu(II) signal [11] causes difficulties in the determination of Cu(II) by anodic stripping analysis even when gallium [20,21] or hydrogen peroxide [22] as a modifier of the deposited species was added. In the positive potential ranges, the carbon-based electrodes [23,24] or gold-film electrodes [25] may be rather effective for the anodic stripping analysis of copper(II).

In the past few decades, different kinds of semiconductors comprised of selenium have received a great deal of attention due to its particular photoelectrical properties and wide applications in electronic and optoelectronic devices such as the solar cell, super ionic conductors, optical filter, etc. In order to obtain an amorphous layer of semiconductor metal-selenide compound, the electrodeposition (electrosynthesis) and characterization have been studied on carbon or gold electrodes [26-29]. Metal selenides (MSe, where M is a divalent cation) are deposited on the working electrode according to the general reaction $H_2SeO_3 + M^{2+} + 6e^- + 4H^+ \rightarrow MSe + 3H_2O$ by a mechanism involving Se^{2-}, selenide, selenious (intermediates) to yield elemental selenium. Copper selenides can play a crucial role of the counterpart for the other metals to be deposited. With respect to electrochemistry of metal selenides, the cathodic stripping voltammetric determination of selenium(IV) has been reported using copper-film mercury and copper-modified mercury-film electrodes, based on the formation of copper selenide compounds [30-32].

When selenium(IV) was added to the solution to a larger content to form the film electrode , we must pay much attention to the metal toxicity and to the storage of the wastes from the view point of environmental protection. The average concentration of seawater, 0.09 mg L^{-1}, is higher than that of mercury. US Environmental Protection Agency recommends to conserve a standard value of 0.01 mg L^{-1} in natural water.

In this article, we report on the polarization character of the *in-situ* prepared selenium film electrode and its successful application for determining traces of Cu(II) in 0.01 mol L^{-1} hydrochloric acid solution by Osteryoung square wave anodic stripping voltammetry (OSWASV). Herein, we demonstrate that an *in-situ* plated selenium-film electrode has been successfully prepared by electroplating technique, and Cu(II) can be determined by anodic stripping voltammetry following preconcentration technique. Regardless of its poor electronic conducting property, the new type of selenium-film electrode can be expected as another “mercury-free” electrode to expand the scope of analytical utilities and applications to trace metal determination in electrochemical stripping analysis.

Experimental

Reagents

All chemicals used were of analytical reagent grade, and all solutions were prepared with deionized and distilled water. Stock solutions of Se(IV) and Cu(II) were individually prepared by diluting 1000 mg L^{-1} standards for atomic absorption spectrometry with 0.01 mol L^{-1} hydrochloric acid. The other metal ion solutions were also prepared by diluting their standard solutions (1000 mg L^{-1}) with 0.01 mol L^{-1} hydrochloric acid. All stock solutions were stored in a refrigerator at 2 °C.

Apparatus

A BAS Model CV-50W voltammetric analyzer (Bioanalytical system, USA) was employed for measurements of cyclic voltammetry (CV) and OSWASV. Unless otherwise stated, the instrumental settings for OSWASV measurements were as follows: 4 mV step potential; 25mV square wave amplitude; 15 Hz frequency; 10 s equilibrium time. A plastic formed carbon disk (PFC, 3 mm in diameter) as working electrode substrate was obtained from BAS (Bioanalytical system, Tokyo, Japan). A platinum wire counter electrode and an Ag/AgCl (sat. KCl) reference electrodes were also used.

Experimental procedures

The plastic formed carbon electrode surface was cleaned by polishing with aluminum oxide slurry and cleaned by distilled water and a piece of filter paper. The treated electrode was then immersed in 1.0 mol L^{-1} hydrochloric acid for 1 min, and rinsed with water. After each voltammetric measurements, the working electrode was cleaned and reactivated by applying the electrode at 800 mV for 60 s in 0.1 mol L^{-1} hydrochloric acid under stirring.

The established procedures for the determination of Cu(II) by OSWASV were set as follows: an aliquot (2.0 mL) of sample solution was introduced into a 15-mL electrochemical cell. The reagent solutions were then added to the standard or sample solution, and the total volume was finally made up to 10.0 mL. The equilibrium concentrations of added reagents except Cu(II) were adjusted to 0.01 mol L^{-1} hydrochloride acid, 0.05 mol L^{-1} potassium chloride, and 500 μg L^{-1} Se(IV). Nitrogen was purged into the solution for 600 s, and then the Cu(II) was initially reduced at a potential of −300 mV for 180 s under solution stirring. After the stirrer was switched off for 10 s equilibrium time, the electrode potential was scanned from −300 to 800 mV in the positive direction.

The standard reference material of river water (SRM JSAC 0302-3 from the Japan Society for Analytical Chemistry) was acidified by 0.01 mol L^{-1} hydrochloride acid. The NBS standard reference material (SRM 1566), oyster tissue (5.00 g), was heated with concentrated nitric acid and hydrochloride acid, and evaporated to almost dryness. The residue was diluted with water (100 mL) to get appropriate concentrations. The reference material samples were analyzed by standard addition and background subtraction method.

Results and discussion

Voltammetric behavior of copper(II) with a selenium-coated carbon electrode

Preliminary experiments indicated that an anodic response due to Cu(II) was observed at about 200 mV vs. Ag/AgCl by applying the working electrode to a positive direction following *in-situ* deposition of copper selenide in presence of excess Se(IV) at −300 mV. Before detailed investigations, the accessible potential range (potential window) of selenium-film carbon electrode was examined by cyclic voltammetric measurements for a blank solution containing 0.01 mol L^{-1} hydrochloric acid and 500 µg L^{-1} Se(IV) over the potential range from −400 to 800 mV (Fig. 1). Since the reduction of Se(0) to Se(-II) appeared as H_2Se occur at potentials lower than −600 mV on a PFC substrate, the cathodic limit was set by the hydrogen generation wave. On the other hand, the anodic limit of Se-film carbon electrode, 400 mV, was set by the oxidation of reduced Se(0) generated *via* the *in-situ* electroplating. The polarization range (potential window) was 1000 mV in 0.01 mol L^{-1} hydrocholoric acid; the anodic limit is more positive than Bi- and Sb-film electrodes due to the more positive oxidation potential of selenium but the polarization range is almost the same as those on both electrodes. A small and broad anodic response, as shown in Fig. 1 (line 2), was observed in the potential range of 200─500 mV for a solution of 500 µg L^{-1} Se(IV) by scanning the potential in a positive direction following deposition at −300 mV for 180 s. On the other hand, Cu(II) itself gives a small response at around –100 mV in absence of Se(IV). The anodic response due to Cu(II) was enhanced at a 5-fold when 500 μg L^{-1} Se(IV) was present (see Fig. 1). As can be seen from Fig. 2, a well-resolved Cu(II) peak at about 200 mV was observed on the OSWASV curve for a test solution containing an excess amount of Se(IV) over Cu(II). Obviously, CuSe and its intermetallic analogues were formed at the deposition step onto the carbon substrate surface, giving rise to a subsequent Cu(II) stripping peak. OSWASV measurements at varying ppb-level concentrations revealed that the peak currents at about 200 mV were directly proportional to the concentration of Cu(II) initially taken (see Fig. 2), which indicates that the proposed OSWASV method enables determination of traces Cu(II) in real samples.

Effect of experimental variables

Several experimental variables have been studied for the determination of 10.0 μg L^{-1} Cu(II) by OSWASV using the *in-situ* plated Se-film carbon electrode. Fig. 3 illustrates the dependence of the Cu(II) response on hydrochloric acid concentration of the test solution. The Cu(II) response increased with increasing hydrochloride acid concentration up to 0.01 mol L^{-1}, and then it decreased from 0.01 to 0.15 mol L^{-1}. We further found that the addition of potassium chloride (0.05 mol L^{-1}) showed maximum over the concentration range of 0-0.30 mol L^{-1}, and that the reproducibility greatly improved. Consequently, a mixed supporting electrolyte of 0.01 mol L^{-1} hydrochloric acid and 0.05 mol L^{-1} potassium chloride was chosen as the most suitable concentrations.

The Cu(II) response increased linearly with increasing Se(IV) concentration up to 300 μg L^{-1}, above which concentrations it remained almost constant (see Fig. 4). The Cu(II) peak potential, on the other hand, shifted to more positive directions with increased concentrations of Se(IV) taken. All subsequent experiments were conducted using a Se(IV) concentration of 500 μg L^{-1} in order to obtain a wider dynamic range of the Cu(II) calibration.

The effect of deposition potential on the Cu(II) anodic response was investigated over the range of −100 to −600 mV vs. Ag/AgCl. The results shown in Fig. 5 indicate that the Cu(II) response was constant in the potential range between −200 and −500 mV. At potentials lower than −500 mV, the anodic response decreased due to formation of H_2Se evolved. Increased deposition times ranging from 60 to 360 s showed a linear relationship with the Cu(II) anodic response. Therefore, a deposition potential of −300 mV and a deposition time of 180 s were chosen in this study.

Calibration curve and detection limit

The calibration plots for the determination of Cu(II) by the proposed OSWASV method were constructed under the optimized experimental conditions. A linear relationship between the OSWASV peak current and Cu(II) concentration was obtained over the concentration range from 1.0 to 100 μg L^{-1}: $I = 0.373C + 1.273$ ($R^2 = 0.9936$, I = peak current in μA; C = Cu(II) concentration in μg L^{-1}). The detection limit calculated as 3σ from a calibration point of 1.0 μg L^{-1} Cu(II) was 0.2 μg L^{-1} for a deposition time of 180 s, and the relative standard deviation was 2.3% (n = 8) for 10.0 μg L^{-1} Cu(II). This detection limit is comparable with those obtained by DPASV methods using the bismuth-film electrodes [22,25].

Interference

The effect of foreign ions on the OSWASV determination of 10 μg L^{-1} Cu(II) by the OSWASV method was investigated at a range of concentrations. The tolerance levels determined within ±10% were 20 μg L^{-1} for Sb(III) and 50 μg L^{-1} for Hg(II), Pb(II), Sn(II), Cd(II) and Mo(VI), respectively. The presence of Bi(II) and As(II) was permissible at 10- and 30-fold amounts excess over Cu(II), respectively. No interference was also observed for Na(I), Mg(II), Al(III), Ca(II), Zn(II), Fe(III), Co(II), Ni(II), Mn(II), V(V) and W(VI) at 1000 μg L^{-1}. Relatively less interferences from most metal ions investigated were observed except for Sb(III). Such anions as NO_3^-, SO_4^{2-} and $H_2PO_4^-$ had no effect at 2.0 mg L^{-1}. We should emphasize that the most remarkable feature of the proposed method is to offer such a better selectivity as well as high sensitivity.

Sample analysis

In order to assess the validity of the proposed OSWASV method, the two reference materials were analyzed by using standard addition method. The procedures for sample pretreatment are the same as those described earlier [14]. Figure 6 shows OSWASV curves obtained by successive addition of standard Cu(II) solution to a diluted sample solution of oyster tissue. The analytical results on four replicate determinations were 9.9 ± 0.2 μg L^{-1} river water (The Japan Society for Analytical Chemistry) and for oyster tissue 64.8 ± 1.6 g g^{-1} (NBS, USA), being coincident with the certified values 9.9 ± 0.1 μg L^{-1} and 63.0 ± 3.5 g g^{-1} respectively. Good accuracy and reliability are shown here; this makes us prompt further developments of possible analytical applications by the electrochemical stripping technique.

Conclusions

The application of the *in-situ* plated Se-film electrode was demonstrated for determining traces of Cu(II) by the proposed anodic stripping method using *in-situ* co-deposition of Se(IV) and Cu(II) onto a plastic formed carbon graphite electrode. The promising characteristic of the Se-film electrode is its wider positive potential range accessible than the Bi- and Sb-films; it rather resembles gold-based electrodes in respect of the polarization range. Thus, this Se film electrode is expected to offer another type of "mercury-free" electrode for stripping analysis of metals or organic materials although it has a poor electronic conducting property.

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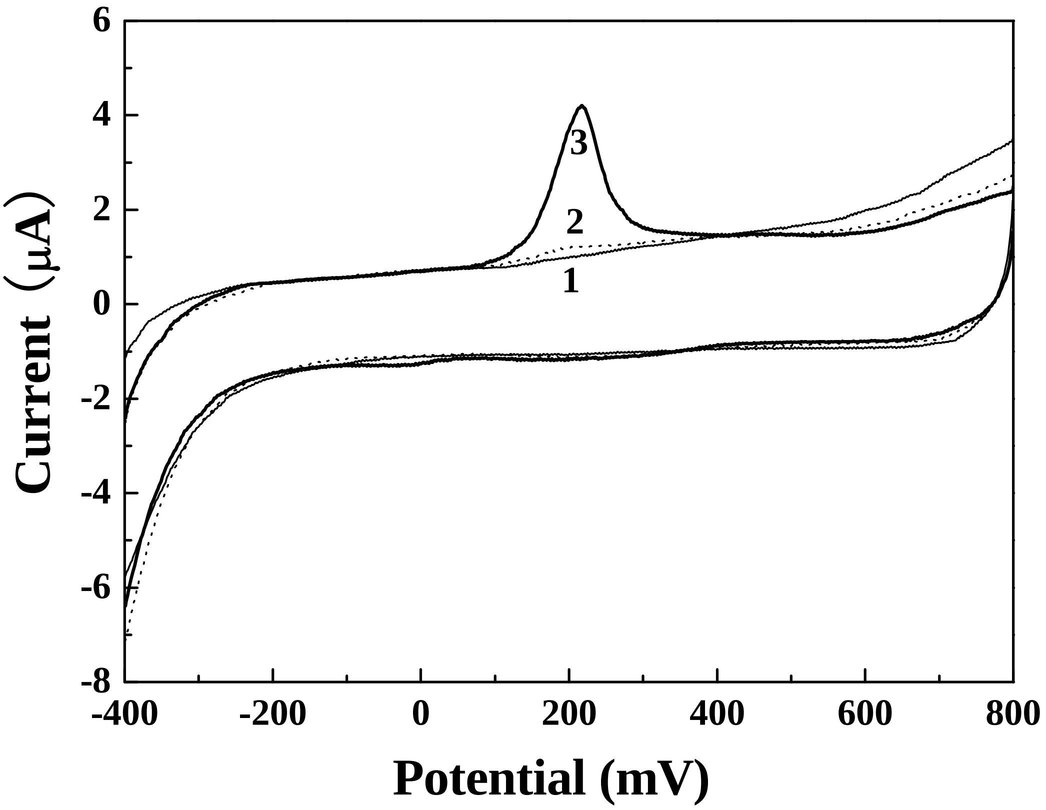

6
4
2
0
-2
-4
-6
-8
Current（μA)
-400
-200
0
200
400
600
800
Potential (mV)
1
2
3

Fig. 1

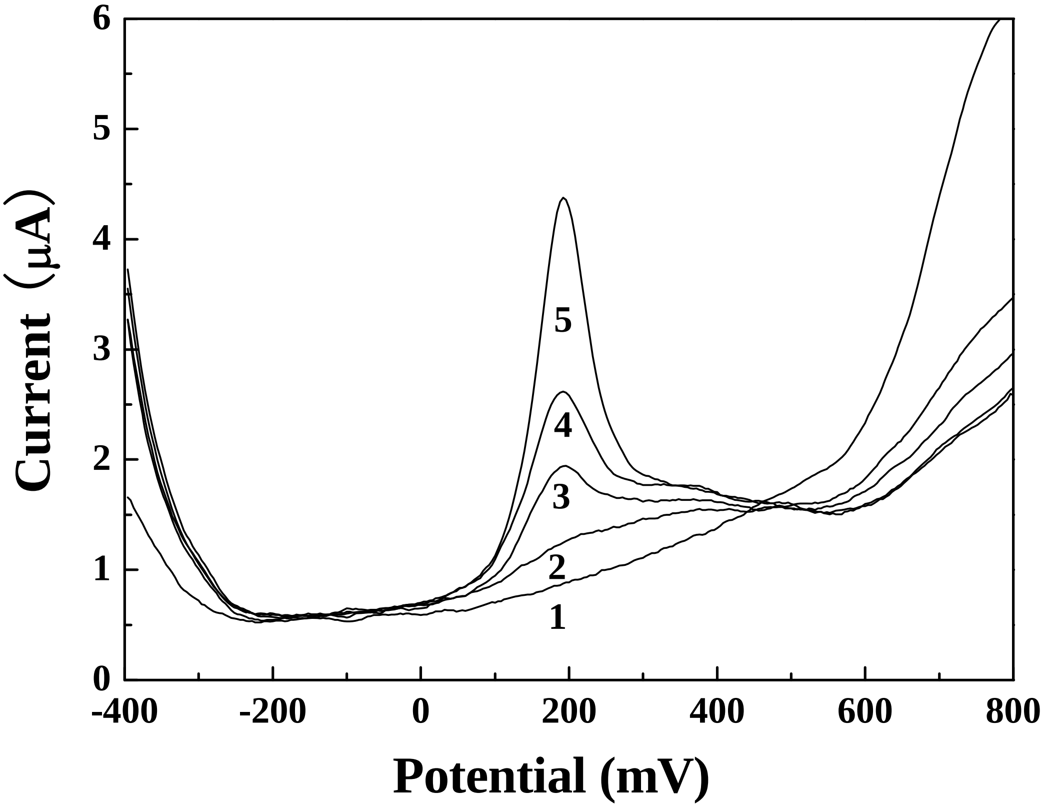

6
5
4
3
2
1
0
Current（μA)
-400
-200
0
200
400
600
800
Potential (mV)
5
4
3
2
1

Fig. 2

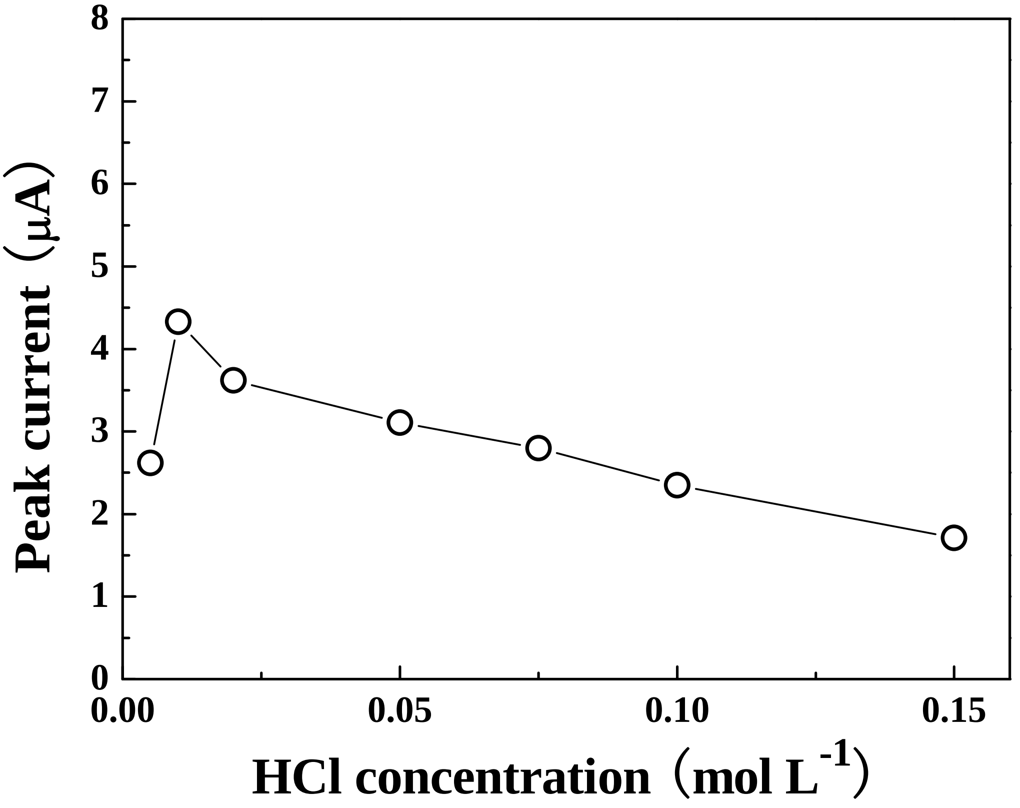
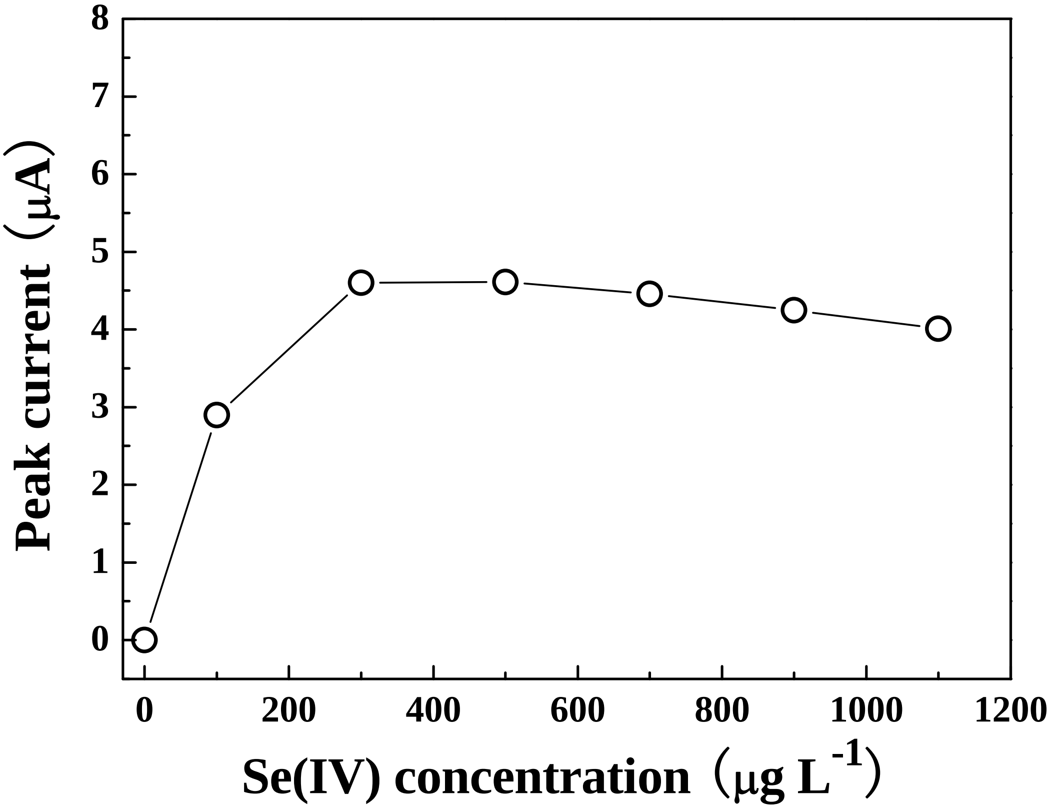

Peak current（μA）
8
7
6
5
4
3
2
1
0
0.00
0.05
0.10
0.15
HCl concentration（mol L-1）

Fig. 3


Peak current (μA)
8
7
6
5
4
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2
1
0
0
200
400
600
800
1000
1200
Se(IV) concentration (μg L-1)

Fig. 4

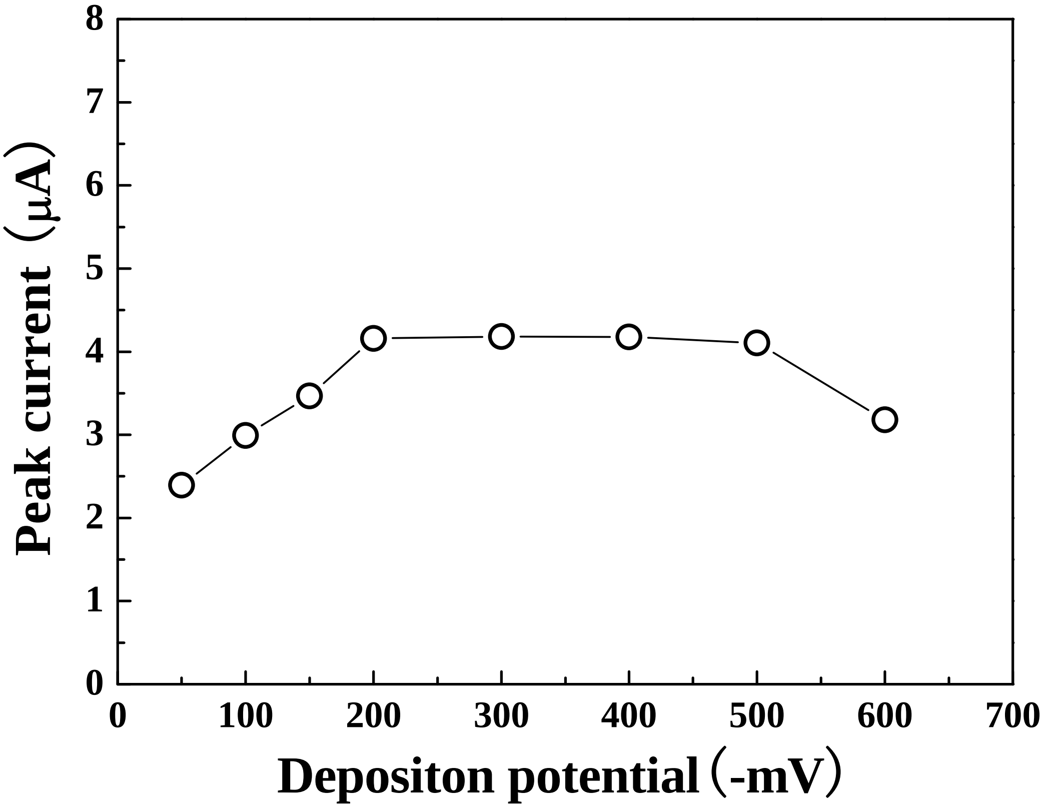
Peak current（μA）
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
Depositon potential（-mV）

Fig. 5

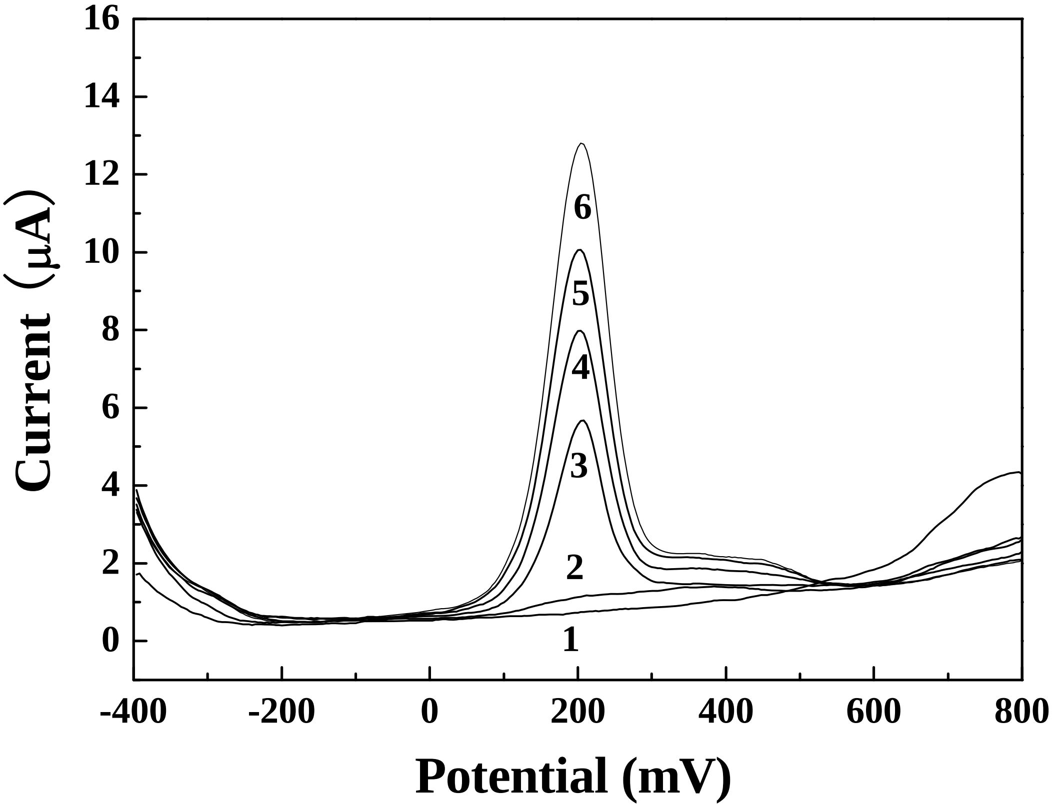
Current（μA)
16
14
12
10
8
6
4
2
0
-400
-200
0
200
400
600
800
Potential (mV)
6
5
4
3
2
1

Fig. 6

Figrue captions

Fig. 1. Cyclic voltammograms. (1) 0.01 mol L^{-1} HCl + 0.05 mol L^{-1} KCl, (2) (1) + 500 μg L^{-1} Se(IV), (3) (2) + 10 μg L^{-1} Cu(II). Deposition potential, -300 mV; deposition time, 180 s; scan rate (mV s^{-1}), 100.

Fig. 2. OSWASV curves. (1) 0.01 mol L^{-1} HCl + 0.05 mol L^{-1} KCl, (2) (1) + 500 μg L^{-1} Se(IV), (3) (2) + 1 μg L^{-1} Cu(II), (4) (2) + 2 μg L^{-1} Cu(II), (5) (2) + 5 μg L^{-1} Cu(II). Deposition potential, -300 mV; deposition time, 180 s.

Fig. 3. Effect of hydrochloric concentration on OSWASV peak current. 500 μg L^{-1} Se(IV) + 10 μg L^{-1} Cu(II). Deposition potential, -300 mV; deposition time, 180 s.

Fig. 4. Effect of Se(IV) concentration on OSWASV peak current. 0.01 mol L^{-1} HCl + 0.05 mol L^{-1} KCl + 500 μg L^{-1} Se(IV) + 10 μg L^{-1} Cu(II). Deposition potential, -300 mV; deposition time, 180 s.

Fig. 5. Effect of deposition potential on OSWASV peak current. 0.01 mol L^{-1} HCl + 0.05 mol L^{-1} KCl + 500 μg L^{-1} Se(IV) + 10 μg L^{-1} Cu(II). Deposition time, 180 s.

Fig. 6. OSWASV curves for Cu(II) determination of Oyster tissue. (1) 0.01 mol L^{-1} HCl + 0.05 mol L^{-1} KCl, (2) (1) + 500 μg L^{-1} Se(IV), (3) (2) + real sample, (4-6) (3) + successive addition of 3 μg L^{-1} Cu(II). Deposition potential, -300 mV; deposition time, 180 s.